STATE LIBRARY OF PENNSYLVANIA
3 0144 00336911 3

CLASS 540.5 BOOK J82511
1931

VOLUME 3

PENNSYLVANIA
STATE LIBRARY

Digitized by the Internet Archive
in 2019 with funding from
This project is made possible by a grant from the Institute of Museum and Library Services as administered by the Pennsylvania Department of Education through the Office of Commonwealth Libraries

https://archive.org/details/vol3industrialen00unse

INDUSTRIAL
and Engineering
CHEMISTRY

ANALYTICAL EDITION

PUBLISHED BY THE
American Chemical Society

VOLUME 3, 1931

Board of Editors

Editor: H. E. HOWE
Assistant to Editor: N. A. PARKINSON

Advisory Board

H. E. BARNARD
J. W. BECKMAN
C. A. BROWNE
C. E. COATES
A. D. LITTLE
A. V. H. MORY
C. L. REESE
G. D. ROSENGARTEN
T. B. WAGNER

EASTON, PA.
MACK PRINTING COMPANY
1931

Analytical Industrial and Engineering Chemistry Edition

Published by the American Chemical Society

Volume 3 JANUARY 15, 1931 Number 1

Estimation of Diastatic Enzyme Preparations[1]

Taka-Diastase, Malt Diastase, and Pancreatic Diastase

Taichi Harada

Department of Biochemistry, New York Post-Graduate Medical School and Hospital, New York, N. Y.

A method is described for the estimation of diastatic power of taka-diastase, malt diastase, and pancreatic diastase. A table for each shows Lintner's value against observed starch titrations. The starch solutions are buffered with acid potassium phthalate and sodium hydroxide solution to give more accurate results than have been previously described. A new standard unit is offered and calculated in terms of Lintner's value. The starch titration is tabulated to show the corresponding glucose content.

The present method is a modification of Lintner's procedure (*3*), being based in principle upon the production of a definite quantity of reducing sugar by the action of a diastase upon a definite amount of Lintner's starch solution under definite conditions. Ling (*2*) has suggested a convenient modification of Lintner's method, but his calculation equation does not represent the true value since the quantity of enzyme used and the amount of sugar produced are not exactly proportional. Recently Oshima (*4*) proposed a table setting forth the relationship between Lintner's value (L. V.) and the amount of starch solution digested by the enzyme which is required to just reduce 5 cc. of Fehling's solution. Lintner's value was obtained experimentally in a series according to the original Lintner method with different strengths of diastatic solutions. In practice the calculation values from Oshima's table do not agree with the right Lintner's value when examined with a different percentage of each enzyme solution of malt and taka-diastase since his starch solution was not buffered (except with a dilute sodium hydroxide solution). The pH value of his starch solution might vary with different percentages of enzyme solution. The isoelectric point of taka-diastase has been found to be at pH 7.0.

It is very necessary to know from time to time the comparative strength of taka-diastase (*Aspergillus oryzae* diastase), malt diastase, and pancreatic diastase for the food and textile world as well as for pharmaceutical purposes in the industrial laboratory. It is also essential to establish a new standard unit for these enzymes under definite conditions. Therefore, the author presents the following method, tables, and unit devised for these three enzyme preparations to the end that more convenient and accurate results may be obtained.

Two other typical methods, those of Wohlgemuth (*7*) and of Sherman, Kendall, and Clark (*5*), are mentioned in the literature, but these are not convenient for industrial laboratory purposes for many reasons. Space does not permit a discussion of them here.

[1] Received June 3, 1930.

256692

Acid Potassium Phthalate and Sodium Hydroxide Buffer Starch Solution

Twenty grams of dry soluble starch (*6*) were suspended in a little cold water in a liter beaker, then about 500 cc. of boiling water were added, and the whole boiled for 2 minutes. After cooling, 250 cc. of acid potassium phthalate and 0.2 *M* sodium hydroxide solution—150 cc. for taka-diastase, 162.5 cc. for malt, and 227 cc. for pancreatic—were added, followed by sufficient distilled water to make 1 liter. One hundred cubic centimeters of this should not completely reduce 5 cc. of Fehling's solution. This solution should be pH 5.2, as tested with chlorophenol red and methyl red. For the enzyme of *Aspergillus oryzae* (taka-diastase) this is the optimum hydrogen-ion concentration under the conditions of this method, but for malt diastase and pancreatic diastase, it should be set at pH 5.3 and 6.0, respectively (*1*).

Enzyme Solution

Exactly 0.05 to 0.5 gram, according to its strength, of finely powdered diastase is weighed out. This is first suspended in 3 to 5 cc. of distilled water in a small glass mortar, then completely dissolved by further addition of water and introduced into a 500-cc. flask by washing with distilled water until the 500-cc. mark is reached (0.01 to 0.1 per cent solutions).

Procedure and Unit

One hundred cubic centimeters of the 2 per cent Lintner's starch solution were introduced into a 150-cc. Erlenmeyer flask by means of a 100-cc. pipet. It was kept in an Ostwald thermostatic bath at 37° C. (± 0.05°) until the starch solution reached that temperature (about 30 minutes) after which 10 cc. of the enzyme solution were added and digestion carried on for exactly 30 minutes at 37° C. At the end of this time, 10 cc. of 0.25 *M* sodium hydroxide solution were added with shaking to stop further reaction. It was removed from the bath and cooled to room temperature. The total starch solution, therefore, should be 120 cc. Fehling's solution is standardized by treating 5 cc. of it with 0.5 per cent

pure glucose solution drop by drop, while boiling, until the Fehling's solution becomes colorless. Five cubic centimeters of the glucose should be required. Some of the digested starch solution is transferred to a buret and gradually run into 5 cc. of the tested Fehling's solution in a test tube. The tube, held in a wire basket, is immersed in boiling water from time to time for about 10 minutes, and then the color is examined. This is continued until the solution just loses its blue color. Thus an approximate volume of the starch solution is ascertained, then the exact volume by repeating the process. When the experiment is carried out with 10 cc. of 1 per cent enzyme solution and it takes just 10 cc. of the starch solution to reduce the standardized Fehling's solution, this is taken as a new standard unit. When 0.12 gram of Lintner's enzyme preparation digested 10 cc. of 2 per cent starch solution so that just enough sugar was produced to reduce exactly 5 cc. of Fehling's solution under definite conditions, he designated this as 100 units. It has been customary to refer to this as Lintner's value (L. V.). The procedure described by the author is equivalent to 120 L. V. It is highly desirable, from a commercial standpoint, to retain the L. V. terminology. The author offers a more satisfactory method for arriving at these values.

Calculations

The enzyme solutions were prepared as follows: A sample of taka-diastase, weighing 0.118 gram and free from sugar, was dissolved in 500 cc. of distilled water. This serves as a stock solution of 0.236 per cent strength. Portions of this were further diluted with increasing amounts of distilled water to make solutions of various percentages. Each solution was treated as described above. The data are given in Table I.

Table I—Lintner's Values against Starch Titration

No. Soln.	Stock Soln.	Added Water	Strength of Starch Soln.	Starch Soln. Required for 5 cc. Fehling's Soln.	Calcd. Value for 1% Enzyme Soln.
	Cc.	*Cc.*	%	*Cc.*	*L. V.*
1	100	0	0.236	3.60	600
2	50	50	0.118	5.25	300
3	30	70	0.0708	7.40	180
4	25	75	0.059	8.50	150
5	20	80	0.0472	10.00	120
6	10	90	0.0236	15.75	60
7	10	190	0.0118	25.00	30
8	10	490	0.00472	40.00	12
9	5	495	0.00236	67.50	6

By definition, if 10 cc. of digested starch solution reduce 5 cc. of Fehling's solution, its Lintner's value is 120 provided its strength is 1 per cent. However, as shown in Table I, solution No. 5 of the enzyme solution is only of 0.0472 per cent strength. Therefore, for 1 per cent of the diastase solution, the true diastatic power of the sample diastase is

$$\text{L. V.}:\text{true L. V.} = \text{per cent of solution}:1 \text{ per cent}$$
$$120:X = 0.0472:1$$
$$X = 2542$$

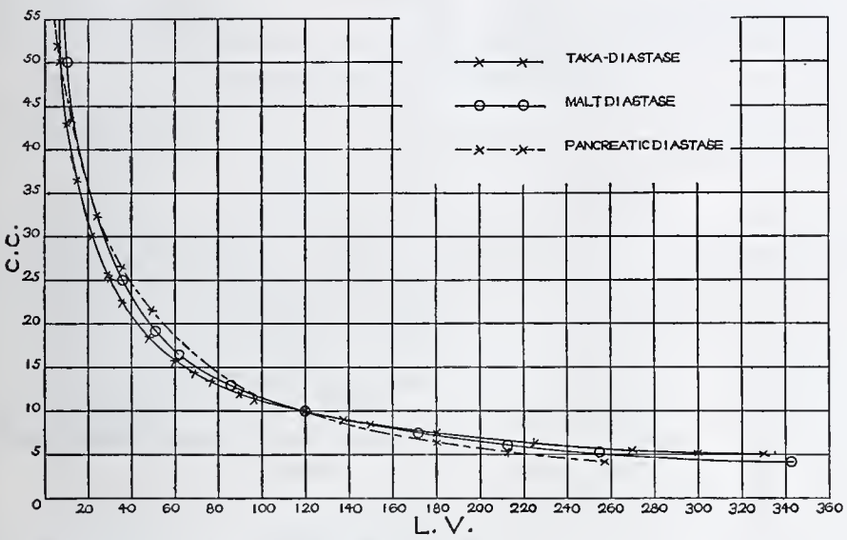
Table II—Lintner's Values of Diastatic Enzyme Preparations against the Starch Titration

Starch Titration	Taka-Diastase	Malt Diastase	Pancreatic Diastase	Corresponding Amount of Glucose
Cc.	*L. V.*	*L. V.*	*L. V.*	%
4.30		343[a]	257[a]	
5.00	332[a]	280	224	0.5000[a]
5.25	300[a]	260	213[a]	0.4750
5.30		257.3[a]		
5.50	271[a]	240	208	0.4500[a]
5.75	254	226	198	0.4330
6.00	240	213[a]	193	0.4160
6.25	225[a]	205	187	0.4000[a]
6.50	214	197	180[a]	0.3880
6.75	203	190	174	0.3760
7.00	192	181	169	0.3625
7.25	182	176	165	
7.35				0.3500[a]
7.40	180[a]			
7.45		171.5[a]		
7.50	176	168	154	0.3380
7.75	169	162	150	0.3280
8.00	162	158	147	0.3185
8.25	155	153	143	0.3075
8.50	150[a]	146	140	0.3000[a]
8.75	143	142	136	0.2925
9.00	138[a]	137	132	0.2835
9.25	133	133	129	0.2750
9.50	129	129	126	0.2680
9.75	124	124	123	0.2615
10.00	120[a]	120[a]	120[a]	0.2550
10.20				0.2500[a]
10.25	114	114	117	0.2480
10.50	111	111	114	0.2430
10.75	108	109	111	0.2370
11.00	104	106	108	0.2320
11.25	100	103	104	0.2275
11.50	97[a]	100	101	0.2230
11.75	94	98	99	0.2180
12.00	90[a]	96	96	0.2150
12.25	88	93	94	0.2115
12.50	85	90	92	0.2070
12.75	82	88	90	0.2030
13.00	80	86[a]	88	0.2000[a]
13.25	79	84	86	0.1975
13.50	77[a]	82	85	0.1925
13.75	75	80	84[a]	0.1880
14.00	73	78	81	0.1850
14.25	70	76	80	0.1825
14.50	69[a]	74	78	0.1775
14.75	67	73	77	0.1760
15.00	65	71	75	0.1735
15.25	63	69	74	0.1710
15.50	62	68	73	0.1680
15.75	60[a]		72	0.1670
16.00	59	65	71	0.1625
16.25	57.5		70	0.1615
16.50	57	62[a]	68	0.1590
16.75			67	0.1570
17.00	54	60	66	0.1550
17.25			65	0.1525
17.50	52	58	64	0.1520
17.75			62	0.1500[a]
18.00	50	56	61	0.1480
18.25			59	0.1470
18.50	48[a]	54	60[a]	0.1450
18.75		53	58	
19.00	46	52	57	0.1415
19.25		51[a]	56.5	
19.50	45	50	56	0.1380
19.75			55	
20.00	43.5	49	54	0.1350
20.25			53	
20.50		47	52	0.1330
20.75			51	
21.00	40	46	50.5	0.1310
21.25				
21.50		44	49[a]	0.1280
21.75				
22.00	37.5		47.5	0.1260
22.25				0.1250[a]
22.50	36[a]	42		
23.00	34.5		44.5	0.1225
23.50		40		0.1210
24.00	32	38	42	0.1190
24.50			40	0.1170
25.00	30[a]	36[a]	39.5	0.1160
25.50	28.6[a]			
26.00	28	34	37	0.1140
26.50			36[a]	
27.00	26	32	34.5	0.1120
27.50				
28.00	25	30	32.5	0.1090
28.50				
29.00	23		30.5	0.1070
29.50		28		
30.00	22[a]	27	28.5	0.1030
30.50				
31.00	21	26	27	0.1010
31.50		25		0.1000[a]
32.00	19.7			0.0980
32.50			24[a]	
33.00		23	23	0.0970
33.50	18			
34.00		22	22	0.0960
34.50	17			
35.00				0.0935
36.00	16	20	20	
36.50	15[a]			0.0900[a]
37.00	14.5			0.0870
38.00		18	17	0.0850
39.00		17.2		0.0835
40.00	12		15	0.0820
41.00	11	16		0.0780
42.00			13	0.0750[a]
43.00	10[a]	14		0.0735
43.50			12[a]	
44.00				0.0725
45.00	9		10.5	0.0715
46.00		12		0.0700
47.00				0.0685
48.00	8		8	0.0670
49.00				0.0660
50.00	7.5[a]	10[a]	7	0.0645
51.00				0.0630
52.00	7		4.8[a]	0.0620
53.00				0.0600
54.00				0.0590
55.00	6.8	8.6		0.0580
65.00				0.0500[a]

[a] Experimental data.

In order to obtain the Lintner's value for 1 per cent enzyme solution for any given solutions, multiply 2542 by per cent of solution.

Table II represents complete data for the three diastases—namely, taka-diastase (A), malt diastase (B), and pancreatic diastase (C)—where the observed titration values were obtained by the above described method. The references (*a*) represent experimental data obtained by repeating with various per cent enzyme solutions. Unmarked numbers are interpolated data obtained from the curve.



Starch Titration against Calculated Values in Terms of L. V. to Per Cent Enzyme Solution

The relations between starch titration and calculated Lintner's values to 1 per cent enzyme solution of these three enzymes are also given in the figure. In testing taka-diastase, the data of Table I may also be used at 50° C. where digestion is carried on under the same conditions except that the starch solution is buffered at pH 5.4 and is made by using 250 cc. of 0.2 *M* acid potassium phthalate and 177 cc. of 0.2 *M* sodium hydroxide solution. The calculation is not altered.

In routine practice it is possible to be more economical and use more dilute buffer solutions—that is, one-fifth of the amount of each buffer solution for the starch solution. Ten cubic centimeters of 0.2 *M* sodium hydroxide solution instead of 0.25 *M* sodium hydroxide are sufficient to stop further reaction.

The last column in Table II gives the percentage of pure glucose which corresponds to the observed starch titration.

Literature Cited

(1) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, 1925.
(2) Euler, "General Chemistry of the Enzymes," p. 290, Wiley, 1912.
(3) Lintner, *J. prakt. Chem.*, **34**, 386 (1886).
(4) Oshima, J. Ind. Eng. Chem., **12**, 991 (1920).
(5) Sherman, Kendall, and Clark, *J. Am. Chem. Soc.*, **32**, 1082 (1910).
(6) Waksman and Davison, "Enzymes," p. 154, Williams and Wilkins, 1926.
(7) Wohlgemuth, *Biochem. Z.*, **9**, 1 (1908).

Quantitative Determination of Potassium by Sodium Cobaltinitrite Method[1]

Pierre J. Van Rysselberge

Stanford University, Calif.

The precipitation of potassium by the sodium cobaltinitrite reagent, studied by de Koninck (*5*), Gilbert (*4*), Adie and Wood (*1*), Cunningham and Perkin (*3*), Vürtheim (*7*), and others, has recently been thoroughly investigated by Bonneau (*2*). The difficulties of the method are reviewed in some of the bulletins of the U. S. Department of Agriculture (*8*).

Bonneau's work confirms the results obtained by Adie and Wood, who showed that the formula of the potassium-sodium cobaltinitrite is $K_2NaCo(NO_2)_6.nH_2O$. According to Bonneau, a constant composition of the precipitate (disregarding the amount of water of hydration) is obtained only if the ratio of the concentration of sodium to that of potassium is larger than 25. Below that ratio the molecule of potassium-sodium cobaltinitrite contains more potassium and less sodium than indicated by the formula given above, the composition tending towards the limiting formula $K_3NaCo(NO_2)_6.nH_2O$. The higher the temperature at which precipitation takes place, the higher the amount of potassium in the molecule. The formula found by Vürtheim is $K_{1.5}Na_{1.5}Co(NO_2)_6.nH_2O$, a result that the work of Bonneau contradicts. Gilbert gives the same formula as Vürtheim. The results of Adie and Wood and those of Bonneau show that the number of water molecules attached to each molecule of $K_2NaCo(NO_2)_6$ is usually one. According to Adie and Wood, drying the precipitate below 130° C. has a negligible influence on the final composition.

After a long series of determinations of potassium in mixed solutions of potassium and sodium chlorides, the writer was able to draw a few interesting conclusions in regard to the sodium cobaltinitrite method, which are presented here as a complement to the work of Bonneau. The reagent was the same as that used by Adie and Wood (*1*). Bonneau (*2*) used cobalt nitrate instead of cobalt acetate.

The writer usually had to determine small changes of concentration of potassium resulting from electrolytic migration (*6*). Those changes were determined by comparing the unknown samples with samples of the original solution for which the amount of potassium was known.

It was necessary to use samples having equal volumes and to add to all of them the same amount of reagent. If, moreover, the time during which the precipitates were allowed to settle was exactly the same for all the samples to be compared, satisfactory results could be obtained. The influence of the time of settling seems to have been overlooked by all the authors who investigated this method, with the exception, perhaps, of Vürtheim. He allowed the precipitates to settle for 18 hours, a time after which no increase of weight of the precipitates could be detected. Adie and Wood let the precipitates settle overnight. Bonneau speaks of "a few hours."

[1] Received July 30, 1930.

With mixtures of potassium and sodium chlorides of a total concentration varying from 0.5 to 5 gram-equivalents per liter, the ratio of the concentration of sodium chloride to that of potassium chloride varying from 9 to 49, the writer obtained ratios of the weight of potassium–sodium cobaltinitrite to the weight of potassium varying from 5.56 to 6.43. The time of settling was at least 4 hours, and in some cases reached 66 hours; in a few exceptional cases ratios in the vicinity of 8 were obtained. The ratio given by Adie and Wood, and Bonneau, corresponding to the formula $K_2NaCo(NO_2)_6.H_2O$, is 5.81 (1:0.172), a ratio which the writer frequently obtained for a time of settling of about 24 hours. The ratio 5.58 corresponds to the formula $K_2NaCo(NO_6)$; the ratio 6.28 to the formula $K_2NaCo(NO_2)_6.3H_2O$.

In general, the weight of the precipitate increases with the time of settling and seems to tend towards a certain limit; the value of that limit and the time after which it is reached are exceedingly variable and seem to depend on the volumes of the samples, their concentration, the way in which the reagent is added, the excess of reagent used, etc. Another point noticed is that, even in the case of low NaCl:KCl ratios, high values of the ratio complex nitrite:K can be obtained. Those high ratios are evidently due to gradual hydration. Samples containing approximately the same amounts of potassium, when treated in strictly identical conditions, usually give identical ratios complex nitrite:K; sometimes, however, differences occur. They correspond as a rule to a variation of 1.3 per cent, which the writer empirically ascribes to a difference of one-third of molecule of water in the composition. Indeed, most of the results could be explained by assuming the formula $[K_2NaCo(NO_2)_6]_3.nH_2O$.

Suggested Method for Determination of Potassium

(1) The reagent is prepared according to the directions of Adie and Wood (*1*). Two solutions having, respectively, the compositions 220 grams of sodium nitrite in 440 cc. of water, 113 grams of cobalt acetate in 300 cc. of water and 100 cc. of glacial acetic acid, are mixed, thoroughly stirred, and filtered just before use.

(2) Several samples, known and unknown, are treated together in exactly the same conditions: the volumes must be the same (independently of the actual amount of potassium they contain, provided the order of magnitude be constant). The same amount of reagent is added to all of them, preferably with a pipet, stirring all the time; this amount should constitute an excess such that, after settling of the precipitate, the supernatant liquid has a dark brown color.

To analyze a solution which contains about 0.1 gram-equivalent of potassium chloride per liter, a 10-cc. sample should be diluted to about 30 cc. and from 20 to 30 cc. of the cobaltinitrite reagent should be used.

The ratios Na:K of the solutions to be analyzed should be of the same order of magnitude for all the samples. The actual value of that ratio is not of primary importance. In order to obtain a constant composition of the complex nitrite, for all concentrations of potassium, one should, after Bonneau (*2*), use a ratio Na:K larger than 25.

(3) The precipitates are allowed to settle for 24 hours. They must all be filtered at the same time, on weighed filters, washed with equal amounts of water acidified with acetic acid, then washed again with alcohol.

(4) The filters are dried, all of them for the same length of time, at about 120° C., then weighed.

(5) The ratio complex nitrite:K is deduced from the analysis of the known samples.

Very satisfactory results are obtained in this way. The accuracy of the method is 1.3 per cent, although in most cases the variations do not exceed a few tenths of one per cent.

Literature Cited

(1) Adie and Wood, *J. Chem. Soc.*, **77**, 1076 (1900).
(2) Bonneau, *Bull. soc. chim.*, **46**, 798 (1929).
(3) Cunningham and Perkin, *J. Chem. Soc.*, **95**, 1562 (1909).
(4) Gilbert, *Z. anal. Chem.*, **38**, 184 (1899).
(5) Koninck, de, *Ibid.*, **20**, 390 (1881).
(6) McBain and Van Rysselberge, *J. Am. Chem. Soc.*, **52**, 2336 (1930).
(7) Vürtheim, *Rec. trav. chim.*, **40**, 593 (1921).
(8) See particularly: U. S. Dept. Agr., *Bur. Chem. Bull.* **137**, **152**.

Micro-Absorption Tube with Mercury Seals[1]

Ralph T. K. Cornwell

National Institute of Health (Hygienic Laboratory), U. S. Public Health Service, Washington, D. C.

THE first absorption tube for organic microcombustions in the determination of carbon and hydrogen, which could be sealed, was designed by Blumer. The Blumer tube is described and discussed by Pregl (*2*). Later a micro-absorption tube was made so that the capillary ends could be sealed by drops of mercury (*1*). An objection to the Kemmerer-Hallett micro-absorption tube is the fragile nature of the ends of the tube. This objection is overcome in the new micro-absorption tube reported here (Figures 1 and 2).

Two[2] hollow glass stoppers were ground to fit the ends of a piece of Pyrex tubing about 14 cm. long and 1 cm. in diameter. The mercury trap and seal were then placed on the inside of the stopper as shown in the diagram. In this way the original straight design of the Pregl micro-absorption tube was retained.

To fill the tube, one of the glass stoppers is attached in the usual manner with Krönig's cement (*3*). A small layer of cotton (about 5 mm.) is then pressed against the stopper and the absorbing material added. This is followed by another layer of cotton and the second glass stopper is sealed to the apparatus in such a manner that the mercury traps in both stoppers occupy the same relative positions. If the Krönig cement is used correctly the ground-glass ends will be transparent. A small drop of clean mercury is then introduced into one end of the tube. This is drawn into the mercury trap by slight suction applied from the Mariotte flask. In the same manner a drop of mercury is placed in the other end. The mercury falls into the two traps, shown in Figure 1, allowing free passage of the gases during the combustion. When the tube is rotated 180 degrees, the mercury falls into the small tubing as shown in Figure 2, and thus protects the

[1] Received August 21, 1930. Publication authorized by the Surgeon General of the U. S. Public Health Service.

[2] The writer wishes to thank Arthur Shroder, director of Technical Service, Fisher Scientific Co., Pittsburgh, Pa., who had an experimental tube made for him. The apparatus can now be purchased from this company.

contents of the tube from the air. Just enough mercury is used to seal the tubes.

The tube for the absorption of water was filled with Anhydrone. Ascarite, followed by 3 to 4 cm. of Anhydrone, was used to absorb the carbon dioxide. Both tubes were kept cool during the combustion by wrapping them in wet flannel. No disadvantage resulted from having one of the sealed glass stoppers next (*4*) to the electric furnace.

Figure 1—Position of Tube during Combustion

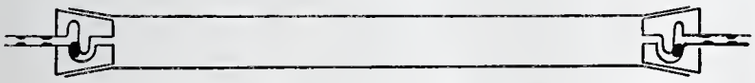


Figure 2—Tube Rotated 180° and Sealed

Following Pregl's directions exactly, but using the new micro-absorption tube, very satisfactory carbon and hydrogen determinations have been made in this laboratory for a period of 6 weeks. Practically theoretical figures can be obtained. One illustration might be of interest: 4.570 mg. (pyrogallol); 1.95 mg. H_2O, 9.583 mg. CO_2. Calcd.: H, 4.79 (8), C, 57.12. Found: H, 4.79 (2); C, 57.19.

The advantages of the micro-absorption tube here described over those already recorded are:

(1) Since both ends can be removed, the cleaning of the tube is greatly facilitated.

(2) While standing on the rack and during the weighing, the tube is sealed—yet, because of the shape it can be wiped before each weighing and handled in the manner so carefully worked out by Professor Pregl.

(3) The tube can be weighed when filled with oxygen or air.

Literature Cited

(1) Kemmerer and Hallett, Ind. Eng. Chem., **19**, 173 (1927).
(2) Pregl, "Quantitative Organic Microanalysis," translated by Fyleman, p. 42, Blakiston, 1924.
(3) *Ibid.*, p. 53.
(4) *Ibid.*, p. 37.

Hydrogen-Ion Determinations with Low-Resistance Glass Electrodes[1]

G. Ross Robertson

University of California at Los Angeles, Calif.

A description is given of glass electrodes which have resistances of but 2 to 3 megohms, and are made of a commercially available glass. Such electrodes permit the use of a d'Arsonval galvanometer in hydrogen-ion estimation with fair accuracy. Their use requires little more skill than is needed with an industrial quinhydrone apparatus. Electrometers are eliminated, and electrostatic shielding becomes of little importance. Directions for construction and use of the apparatus are given.

The estimation of hydrogen ion by standard methods becomes difficult or impossible when the solution under examination contains certain active oxidizing or reducing agents. In such situations the glass electrode invites consideration. Although this device has been known for over twenty years (*2*), it has been generally overlooked in American laboratories. Thanks largely to the recent work of MacInnes and Dole (*4*, *5*), and Elder and Wright (*1*), it is now attracting considerable attention.

A serious drawback of the glass electrode has been its very large electrical resistance. Values of 20 to 100 megohms are commonly reported in the literature. When such a device is placed in the ordinary potentiometer circuit in place of the common hydrogen or quinhydrone electrode, the current becomes too small for detection on a common galvanometer at adjustments near the null point.

A quadrant electrometer, or vacuum-tube potentiometer (*1*), is accordingly used instead of the galvanometer. More or less electrostatic shielding and special insulation are necessitated in such apparatus. In any case the exacting technic required in the use of these physical instruments is discouraging to an ordinary chemist who is seeking only an approximate estimation of pH value.

In the present work the resistance of the electrodes was cut to values from 2 to 3 megohms, the bulbs being blown thin. It was then found that Leeds and Northrup type R galvanometer, model No. 2500-f, an instrument of moderate cost, became useful. This galvanometer, while not of precision grade, has a sensitivity of 0.0001 microampere. It may accordingly be connected and used in a glass electrode apparatus in the same manner which one would employ with a quinhydrone electrode. Furthermore, since the resistance of the glass electrode is so low, static charges do not accumulate and disturb the galvanometer as they do an electrometer which by its very nature has no current "leak."

The sharpness of estimation of the null point is of course not so great as in a common potentiometer circuit in a hydrogen-ion determination. It is, however, sufficient to serve ordinary purposes, as seen in the following illustration:

Assume 3 megohms resistance, and the normal galvanometer deflection of 1 mm. for 10^{-10} amperes current. Suppose the potentiometer adjustment has come within just one millivolt of the null point. The current which is to actuate the galvanometer upon depression of the contact key is, therefore, by Ohm's law

$$\frac{0.001}{3 \times 10^6} = 3 \times 10^{-10} \text{ amperes}$$

Such a current deflects the No. 2500-f galvanometer marker 3 mm., and thus one may locate the null point to the accuracy of one millivolt with ease. This indicates a maximum error of ± 0.02 pH in this part of the operation. On account of the relatively long period of the galvanometer any greater precision in estimation requires more time than one would care to take in rapid commercial work.

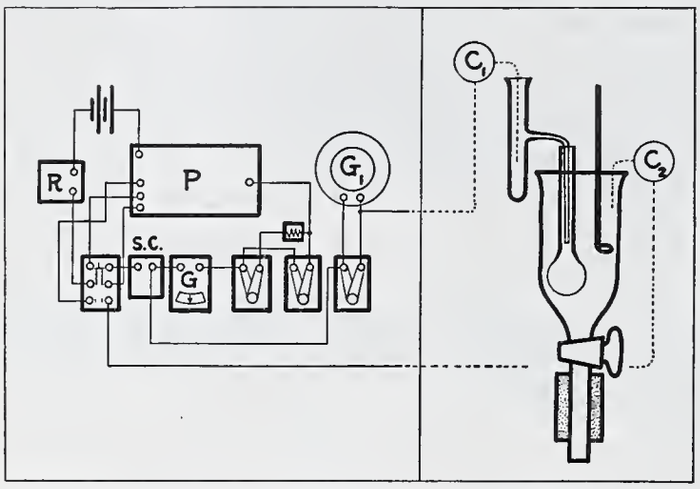
Preparation of Electrode

Corning No. 015 glass, as suggested by MacInnes and Dole (*5*), proved to be suitable for the purpose. It is obtainable from the manufacturer. A piece of 10-mm. tubing of this

[1] Received May 23, 1930.

glass, about 8 cm. long, is drawn to a tapering point in a flame. With the aid of a needle-pointed blast flame a small lump of molten glass of about 100 to 150 mg. weight is allowed to accumulate. Care is taken not to heat the glass to a temperature where gas bubbles are formed.

While the tip is at a bright red heat the tube is quickly removed from the flame and held point down. A bulb of 8 to 10 cc. volume is now blown. Experience alone will show how the air pressure may be controlled to prevent a blowout and give a very thin bulb of good mechanical strength. The writer has success when he restrains the blowing until the bulb, half blown, is getting almost too cool, and then by one hard blow stretches it to full size. This trick involves the



Apparatus for Hydrogen-Ion Determinations

"setting" of portions of the bulb which are already as thin as they should be, and the further spreading of other portions which are still hot enough to spread. A large part of the bulb thus becomes thin enough to conduct the electric current freely in the application to follow. Such technic will sometimes give slightly lopsided bulbs, which are nevertheless serviceable.

After the electrode is cool, its open end is dipped momentarily into melted paraffin as deeply as may be necessary to protect the section which is to be held by a clamp on the supporting stand.

The following measurements were made of one particularly good electrode of 2 megohms resistance:

Volume of bulb section of electrode	8.5 cc.
Surface area of thin, or useful part of bulb, approx.	14 sq. cm.
Average thickness of wall	0.03 mm.
Variation in thickness	0.015 to 0.05 mm.

Arrangement of Apparatus

The whole cell and stirrer assembly, as shown in the right section of the figure, is mounted securely on one large ring-stand to insure rigidity and protection of the bulb.

Calomel electrode C_1 dips into a test tube filled with dilute potassium chloride solution. The slender side stem of this test tube is filled with potassium chloride–agar jelly, and dips into the reference solution of hydrochloric acid (approx. 1 N) in the glass electrode. Calomel electrode C_2, presumably identical with C_1, dips into the solution under examination, placed in the main vessel. A mechanical stirrer is included.

G_1 is the type R galvanometer provided with a special tapping key used to stop the motion of the coil. This key merely serves to short-circuit the galvanometer temporarily. Some workers may prefer to include a damping resistance of from 2000 to 10,000 ohms in the key circuit, in case a retardation of the coil is desired instead of instant stoppage.

A convex lens is placed directly in front of the galvanometer mirror, and the image of a straight-line-filament incandescent lamp thus projected on an external scale.

The rest of the apparatus is Leeds and Northrup's student potentiometer outfit with slight changes in wiring to accommodate a second galvanometer.

Manipulation

Assuming that 1 N hydrochloric acid is in the bulb, the solution of unknown pH value is placed in the main vessel. The operator then proceeds to determine the potential just as though a hydrogen or quinhydrone electrode were in place of the glass-calomel electrode. The damping key is used freely to stop impending wide deflections and bring the galvanometer to rest promptly.

It is not advisable to attempt a calculation of pH value simply from the concentration of the hydrochloric acid and the known potential—a procedure which is correct in simple theory. Unfortunately such calculations are vitiated by glass surface potentials. The surface potential is not predictable, will change during the day, but will remain fairly constant over the few minutes required for a determination. It is thus advisable to ignore the numerical value of hydrogen-ion activity in the bulb. The plan then is to determine the potentials with three solutions: the unknown, one buffer solution of higher pH value, and one of lower. Direct linear interpolation gives a value sufficiently accurate for many industrial uses. The following example, taken from a rapid determination without thermostat or special refinement of technic, illustrates results obtainable in this manner:

A solution of commercial acid potassium phthalate (approx. 0.2 M), and a standard buffer solution (pH 5) were taken as unknowns. The pH value of each was estimated in reference to two standard buffers, pH 3 and pH 7. The potentials at 29° C. were as follows:

	Volt
Standard buffer pH 3	0.097
Acid potassium phthalate	0.164
Buffer pH 5	0.215
Standard buffer pH 7	0.331

Interpolation between standard buffers 3 and 7 assigns a pH value of 4.1 to the phthalate, and of 5.0 to the intermediate buffer. The apparent potential interval per pH unit between 3 and 5 was 0.059, and between 5 and 7 was 0.058.

Precautions

The three determinations of potential required in the estimation of a pH value should be run off in rapid succession. In such a case the glass potential will be constant, and can be ignored in calculation, as only the concentration potential will enter into the numerical values gotten by interpolation.

Furthermore, the electrode should not be subjected to any unusual disturbance at or near the time of the potential measurements. This advice means constancy in temperature as a prime requirement. Apparently sudden changes in temperature not only cause the small changes in potential called for by electrometric theory, but also may stimulate glass potential drift of unknown magnitude. It is not advisable to permit the electrode to come in contact with a very concentrated acid or alkali at a time near that of a regular series of three measurements. Undoubtedly the most accurate performance of this apparatus will come in a situation where pH measurements are made continuously in one fairly narrow region; where the electrode does not come into contact with a changing variety of electrolytes; and where temperatures are constant within a half degree or better.

Polarization

It was feared that an attempt to draw enough current from a glass electrode to actuate an energy-consuming instrument such as a galvanometer would polarize the electrode and throw

potential readings astray. Experiments have shown, however, that no measurable error is recorded even after the contact key has been closed for a full minute, unless the potentiometer is set much more than 20 millivolts off the null point. Even when the setting was as much as 100 millivolts off the null point the potential returned to normal within a few seconds of rest. Such abuse should not occur in practice; in fact, it would actually send the galvanometer marker entirely off the scale, twist the suspension, and require a new zero setting. It is likely that the increase in conductivity provided in these electrodes has brought an increase in resistance to polarization with a given current flow.

It was noted, however, that in cases where the electrode was polarized with large currents it did not return to normal potential as rapidly as would a quinhydrone electrode. Obviously one should avoid long periods of key contact.

Silver–Silver Chloride Electrodes

Some workers may prefer to use the silver chloride electrode in place of the calomel electrodes here described. In this way one might eliminate the potassium chloride–agar bridge which, though simple and easy to prepare, is not permanent. The silver electrode would be placed directly in the glass electrode bulb. Details of the silver electrodes have been given by MacInnes and Beattie (*3*) and MacInnes and Dole (*4*).

Acknowledgment

The writer wishes to thank James B. Conant, and also the Corning Glass Company, for suggestions and materials in connection with this work.

Note—Since the writing of the foregoing account, an abstract [*C. A.*, **24**, 4188 (1930)] has been published giving a report of the work of C. Morton with glass electrodes of character similar to those described above, but with different electrical accessories and technic.

Literature Cited

(1) Elder and Wright, *Proc. Natl. Acad. Sci.*, **14**, 936 (1928).
(2) Haber and Klemensiewicz, *Z. phys. Chem.*, **67**, 385 (1909).
(3) MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1118 (1920).
(4) MacInnes and Dole, Ind. Eng. Chem., Anal. Ed., **1**, 57 (1929).
(5) MacInnes and Dole, *J. Am. Chem. Soc.*, **52**, 29 (1930).

Methods for Determining the Solubilities of Some Fluosilicates[1]

Katherine K. Worthington with Malcolm M. Haring

University of Maryland, College Park, Md.

THE fluosilicates have recently attracted considerable attention due to their use as insecticides and fungicides, in waterproofing and hardening concrete, in electroplating, etc. However, quantitative data in connection with these substances are not numerous and usually of questionable accuracy. Carter (*2*) has recently published the solubility curves for barium, potassium, and sodium fluosilicates, together with a compilation of all available solubility figures on the fluosilicates. Methods of analysis, likewise, are not all that might be desired.

This paper presents the solubilities and densities, both at 20° C., of the fluosilicates of sodium, magnesium, zinc, lead, and copper. It includes also a brief discussion of the analytical methods.

Apparatus

The apparatus deemed most suitable for the purpose was that of Bahr (*1*). The air used for stirring was first passed through a mercury pressure regulator, by which the rate of flow was maintained constant at 4 bubbles per second. Thence it passed in succession through three Drechsel gas-washing bottles (equipped with petticoat bubblers) containing sodium hydroxide solution, water, and the solution being saturated. Tests showed that the air current produced no decomposition of the fluosilicates above that taking place when the air stream was stationary. Saturator and pycnometer were arranged exactly as described by Bahr, save that a single three-way cock was used in place of two ordinary cocks. A small test tube equipped with an air vent was attached to the pycnometer so as to catch the overflow produced during filling. The whole apparatus was connected by means of ground-glass joints covered with rubber tubing and was completely immersed in an automatic thermostat adjusted to ±0.5° C. No leakage through the submerged joints was observed at any time. A small filter of packed asbestos fiber was formed in a conical tube inserted between saturator and pycnometer. The solutions, after passing the filter, were always absolutely clear. A Sprengel pycnometer of about 6.8 cc. capacity was used. All weights and volumetric apparatus were carefully calibrated. Nearly saturated solutions were made in a flask before placing in the saturator. At least 2 hours were allowed to elapse before the first sample was removed from the saturator. Successive samples never showed any trend in analysis.

Analytical Methods

The fluosilicates have the general formula $Met(SiF_6)$. The water of crystallization varies from 0 to 6 molecules. They are efflorescent and also decompose slowly, especially those of the heavy metals.

They are all decomposed rapidly by hot sulfuric acid and by hot sodium hydroxide as follows:

$$MetSiF_6 + H_2SO_4 = MetSO_4 + SiF_4\uparrow + 2HF\uparrow \quad (1)$$
$$MetSiF_6 + 4NaOH = 4NaF + 2H_2O + SiO_2\downarrow + MetF_2 \quad (2)$$

The first reaction is quantitative and the second may or may not be, depending on the extent of hydrolysis, etc.

Hydrolysis is very slight in the case of the alkali fluosilicates, but more marked with the others—e. g., $MgSiF_6$.

$$MgSiF_6 + 2H_2O = Mg(OH)_2\downarrow + 2H_2SiF_6 \quad (3)$$
$$H_2SiF_6 + 6NaOH = 6NaF + SiO_2\downarrow + 4H_2O \quad (4)$$

Since the methods of analysis used are based on Reactions 1 and 2, it is obvious that hydrolysis will occasion an error in the results when Reaction 2 is used. Reaction 2 requires 4 mols of alkali per mol of fluosilicate whereas Reaction 4 requires 6 mols. Hence volumetric methods of estimation

[1] Received August 29, 1930. Abstracted from a thesis submitted by Katherine K. Worthington in partial fulfilment of the requirements for the degree of master of science in the Graduate School of the University of Maryland.

for fluosilicates that hydrolyze must be viewed with suspicion. The degree of hydrolysis varying with temperature and concentration, it is obvious that variable results are likely to be observed. This accords exactly with the writers' experience.

When the fluosilicates of amphoteric substances are studied, volumetric methods become still more dubious. Consider $ZnSiF_6$:

$$ZnSiF_6 + 4NaOH = ZnF_2 + 4NaF + 2H_2O + SiO_2\downarrow \quad (5)$$
$$ZnF_2 + 2H_2O = Zn(OH)_2\downarrow + 2HF \quad (6)$$
$$HF + NaOH = NaF + H_2O \quad (7)$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O \quad (8)$$

The extent to which Reactions 6 and 8 proceed depends on temperature, concentration, and H-ion concentration.

For these reasons the first method of analysis was used with zinc, lead, and copper fluosilicates. The sample of fluosilicate was heated to vigorous fuming with sulfuric acid containing a little nitric acid. No trace of silica was observed after this treatment. When cool, the trace of iron usually present was precipitated with ammonium hydroxide and filtered off, thus leaving a pure metal sulfate solution for appropriate analysis.

Owing to hydrolysis, free acid figures on the salts are not particularly valuable except to show the magnitude.

The method used by the writers, that of Jacobson (*4*), consists in adding ice and an excess of potassium chloride, then titrating with sodium hydroxide.

$$H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl \quad (9)$$
$$HCl + NaOH = NaCl + H_2O \quad (10)$$

Phenolphthalein was used as indicator with sodium and magnesium fluosilicate and methyl red with zinc fluosilicate.

Preparation and Analysis of Salts and Data

Hydrofluosilicic Acid—This was a very pure and concentrated acid obtained as condensate from the gas tunnel from the hot dens of a phosphate rock acidulating plant.

Sodium Fluosilicate—This salt was prepared in two ways:

(1) Nearly the theoretical amount of the purest sodium chloride was added to a solution of fluosilicic acid containing 100 grams of the acid per liter. Precipitation was immediate. To prevent the formation of a gel, the mother liquor was filtered off immediately and the crystals were washed with cold water on the filter. They were then dried at room temperature.

(2) The procedure was the same as under (1) save that acid sodium carbonate was added slowly.

The crystals made by the first method analyzed 100.05 per cent Na_2SiF_6, those by the second method, 99.41 per cent. Crystals made by the first method were used in the solubility determinations. They were fine, white, and opaque. No free acid was found. The solution was titrated hot with sodium hydroxide, using phenolphthalein as indicator. Carter (*2*) found 0.690 per cent (by interpolation from his table).

The results on this and the other salts will be found in Table I. Each value represents the mean of from four to thirteen determinations.

Table I—Solubilities of Some Fluosilicates at 20° C.

Salt	Specific Gravity 20°/4° C.	Solubility	Av. Deviation from Mean
		%	%
Na_2SiF_6	1.0054	0.733	±0.002
$MgSiF_6.6H_2O$	1.2395	37.94	±0.29
$ZnSiF_6.6H_2O$	1.4336	49.94	±0.23
$PbSiF_6.4H_2O$	2.4314	81.90	±0.1
$CuSiF_6.4H_2O$	1.6174	59.08	±0.11

Magnesium Fluosilicate—A very pure commercial product was used as the source of this salt. Recrystallization did not improve the purity. The salt was made by dissolving magnesite in a slight excess of dilute fluosilicic acid, evaporating at 77° C. with agitation, allowing the silica to settle out, and crystallizing at 41° C. under reduced pressure. The crystals were dried in a rotary drier. The salt analyzed 101.53 per cent $MgSiF_6.6H_2O$. The free acid was found to be 0.83 per cent. Magnesium fluosilicate forms large, water-clear crystals. Its saturated solution is slightly viscous. Although hydrolysis is not excessive, the fluosilicic acid and magnesium hydroxide are quite gelatinous and make filtration difficult.

The solutions were analyzed volumetrically in the same way as the sodium fluosilicate solutions. As a check magnesium was determined gravimetrically as the pyrophosphate according to the method described by Scott (*5*).

The volumetric results are so much more concordant that it seems safe to accept them as final. The tediousness of the gravimetric method is probably responsible for the differences observed. Only the volumetric results are given.

Zinc Fluosilicate—The zinc fluosilicate likewise was a very pure commercial product. It was made in the same manner as the magnesium fluosilicate, except that zinc oxide was used instead of magnesite. The analysis was 95.58 per cent $ZnSiF_6.6H_2O$. The crystals contained 0.79 per cent free acid. The crystals in appearance resemble those of the magnesium salt. The saturated solution is quite viscous. However, filtration is relatively easy, since the hydrolysis products are not very gelatinous.

For reasons already advanced, the volumetric method of analysis is not feasible with this salt. The zinc was therefore precipitated as $ZnNH_4PO_4$ in neutral solution and ignited and weighed as the pyrophosphate. The method of Fales and Ware (*3*) was used on several samples and found to give results identical with the pyrophosphate method. The data given are based on the latter method.

Lead Fluosilicate—This salt was prepared by adding about 10 per cent less than the theoretical amount of red lead to a dilute fluosilicic acid solution. Strong acid produces too much decomposition of the salt because of the excessive rise in temperature. Silica and lead dioxide are formed in the reaction and must be filtered off. The solution so formed was allowed to crystallize at room temperature. The crystals analyzed 99.96 per cent $PbSiF_6.4H_2O$. This high purity was probably due to the insolubility of lead fluoride.

Lead fluosilicate is the most unstable of all those studied. Slow thermal decomposition proceeds even at room temperature. In consequence the dry salt and its solutions are very corrosive. The crystals are large, clear, and highly refractive. If allowed to stand exposed to the air, they become opaque. The saturated solution is very viscous and hydrolyzes slowly on standing, with the formation of an opaque, white precipitate.

Volumetric methods cannot be used in the analysis of these solutions, so the lead was precipitated as the chromate according to Scott (*5*). When the saturated solution was diluted, a precipitate formed which was cleared up with nitric acid.

Copper Fluosilicate—This salt was prepared in four different ways:

(1) 10 per cent fluosilicic acid solution plus about 10 per cent less than theoretical C. P. cupric oxide.
(2) Same as (1) but using C. P. basic copper carbonate.
(3) and (4) Same as (1) and (2) but using 30 per cent acid.

Recrystallization of the product formed by each one of the four methods gave crystals identical in all their properties. Crystallization and drying were carried out at room temperature. The crystals are a clear, sparkling blue and are quite

efflorescent. They must be preserved in a carefully stoppered bottle. The saturated solution is viscous. The crystals used analyzed 99.95 per cent $CuSiF_6.4H_2O$. Copper was determined iodometrically according to Scott (*5*).

Acknowledgment

Thanks are due to G. C. Connolly for advice and supervision during the progress of this work and to the Davison Chemical Company for the use of their analytical laboratory.

Literature Cited

(1) Bahr, *Z. anorg. Chem.*, **71**, 85 (1911).
(2) Carter, Ind. Eng. Chem., **22**, 886 (1930).
(3) Fales and Ware, *J. Am. Chem. Soc.*, **41**, 487 (1919).
(4) Jacobson, *J. Phys. Chem.*, **27**, 577, 761 (1923); **28**, 506 (1924).
(5) Scott, Standard Methods of Chemical Analysis (1925).

Device for Estimation of Density of Gems and Small Amounts of Solids[1]

Eugene W. Blank

Allentown, Pa.

IT IS frequently eminently desirable to determine rapidly the density or specific gravity of small amounts of solids too minute to be determined by the more usual methods available to the investigator. The device to be described is particularly adapted for the determination of the density of extremely small quantities of substances, cut gems, and small mineral crystals or fragments.

There are several methods available for the determination of the density or specific gravity of solids (*4*). These involve the use of: (1) the chemical balance, (2) the pycnometer, (3) heavy liquids and the Westphal balance, and (4) the Jolly balance.

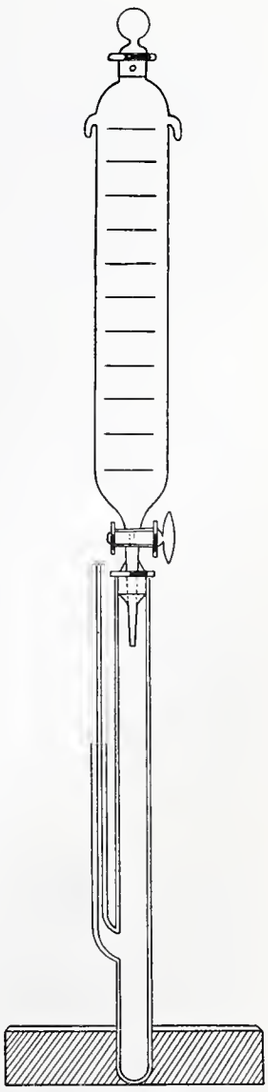
These methods, with the possible exception of the third, are not adaptable to small amounts of solids. The use of heavy liquids is time consuming and the limit of accuracy seems to be 0.03 (*5*). Furthermore many substances are encountered with a higher density than the heaviest liquid obtainable. The use of a wax and red lead float or the use of clips with small specimens is not compatible with accuracy (*7*). Caley (*1*) has perfected an ingenious instrument for the determination of densities that is both accurate and rapid, but not adaptable for substances lighter than the displacing liquid nor specimens it is not desirable to crush, as in the case of gems.

The principle of this device is relatively simple. A narrow tube is filled with a suitable liquid to a mark on a side capillary tube. The sample is inserted in the liquid, and more liquid added from a weight buret to bring the liquid level with a second mark on the capillary tube. The weight of liquid required to fill the instrument from the lower mark to the higher one is previously determined. By subtracting the weight of liquid required to bring the volume from the first to the second mark when the sample is in the tube, from the weight required when the instrument is empty, gives the weight of liquid displaced by the specimen. Since the density of the liquid is known the volume of the specimen can be obtained by a simple calculation, and this value divided into the weight of the specimen gives the desired density.

The method is simple, relatively rapid, and quite accurate.

Description of Instrument

The device is constructed of glass and is 12.0 cm. in height with an internal diameter of 0.6 to 0.8 cm. The base may be a glass or wooden block with a single hole large enough to hold the inserted tube upright. The capillary tube has an internal diameter of 1.0 mm. and should widen gradually to the point of attachment to the main body of the instrument to prevent the inclusion of air bubbles when the instrument is being filled with liquid. It is important that the internal diameter of the capillary shall not exceed 2.0 mm. or be smaller than 1.0 mm. A larger diameter means loss of accuracy when the specimen is very small while a smaller diameter leads to difficulties due to the inclusion of air bubbles when filling the instrument. The capillary should rise to a considerable height, 3.0 to 4.0 cm., above the highest liquid level in order that loss of liquid by evaporation and consequent loss in accuracy may be reduced to a minimum. It has been found by experiment that loss due to evaporation in the capillary under these conditions is negligible over short periods of time. A small weight buret was designed for the instrument bearing in mind several advantages mentioned by Friedman and LaMer (*3*). However, any weight buret of small size is adaptable to this instrument. It is essential that the buret be fitted with a glass cap and the ground surface for the cap should securely fit the top of the instrument to prevent any loss by evaporation when using very volatile liquids for displacement.



Device for Estimation of Density of Gems and Small Amounts of Solids

Displacement Liquids

Water may be used as the displacement liquid for relatively large specimens. In this case the capillary should be at least 1.5 mm. in internal diameter to prevent the inclusion of minute air bubbles. With very small specimens the high surface tension of water causes errors due to the inclusion of air bubbles on the surface and between the particles of solid sample. The most satisfactory displacement liquid is ethyl ether but correct results are obtained only by careful attention to the proper method of using the apparatus. With ethyl ether any minute air bubbles adhering to the surface of the specimen may be readily liberated by

[1] Received September 19, 1930.

Table I—Estimation of Densities of Several Semi-Precious Gems

Sample	Displaced Ether Weight	Displaced Ether Volume	Density Found	Density Pycnometer
Grams	*Gram*	*Cc.*		
		BERYL, AQUAMARINE: RUSSIA		
2.1318	0.5721	0.7957	2.68	
	0.5700	0.7928	2.69	
	0.5760	0.8011	2.66	
	0.5743	0.7987	2.67	
			Av. 2.68	2.68
		BERYL, AQUAMARINE: BRAZIL		
1.1730	0.3183	0.4427	2.65	
	0.3152	0.4384	2.68	
	0.3177	0.4419	2.65	
	0.3197	0.4446	2.64	
			Av. 2.66	2.65
		TOURMALINE: JAPAN		
1.9470	0.4553	0.6332	3.07	
	0.4546	0.6323	3.08	
	0.4578	0.6367	3.06	
	0.4598	0.6395	3.04	
			Av. 3.06	3.06
		APPLICABILITY OF METHOD TO SMALL QUANTITIES OF SAMPLE		
		BERYL, AQUAMARINE: RUSSIA		
0.3467	0.0943	0.1312	2.64	
	0.0932	0.1296	2.68	
	0.0958	0.1332	2.60	
	0.0936	0.1302	2.66	
			Av. 2.65	2.68
		BERYL, AQUAMARINE: BRAZIL		
0.1864	0.0519	0.0722	2.58	
	0.0507	0.0705	2.64	
	0.0498	0.0693	2.69	
	0.0505	0.0702	2.66	
			Av. 2.64	2.65
		TOURMALINE: JAPAN		
0.1191	0.0283	0.0394	3.02	
	0.0278	0.0387	3.08	
	0.0287	0.0399	2.98	
	0.0280	0.0389	3.06	
			Av. 3.04	3.06

Table II—Estimation of Densities of Several Crystallized Minerals

Sample	Displaced Ether Weight	Displaced Ether Volume	Density Found	Density Pycnometer
Grams	*Gram*	*Cc.*		
		CASSITERITE: BOHEMIA		
4.4516	0.4594	0.6389	6.97	
	0.4602	0.6401	6.95	
	0.4611	0.6413	6.94	
	0.4590	0.6384	6.97	
			Av. 6.96	6.96
		CORUNDUM: CANADA		
3.9721	0.7206	1.0023	3.96	
	0.7211	1.0029	3.96	
	0.7200	1.0014	3.97	
	0.7197	1.0010	3.97	
			Av. 3.97	3.96
		ORTHOCLASE: MONTANA		
3.1673	0.8916	1.2401	2.55	
	0.8914	1.2398	2.55	
	0.8926	1.2414	2.55	
	0.8920	1.2406	2.55	
			Av. 2.55	2.55
		APPLICABILITY OF METHOD TO SMALL QUANTITIES OF SAMPLE		
		CASSITERITE: BOHEMIA		
0.3015	0.0310	0.0431	7.00	
	0.0314	0.0437	6.90	
	0.0312	0.0434	6.95	
	0.0312	0.0434	6.95	
			Av. 6.95	6.96
		CORUNDUM: CANADA		
0.2143	0.0391	0.0544	3.94	
	0.0388	0.0540	3.97	
	0.0379	0.0527	4.07	
	0.0390	0.0542	3.95	
			Av. 3.98	3.96
		ORTHOCLASE: MONTANA		
0.1569	0.0449	0.0624	2.51	
	0.0447	0.0622	2.52	
	0.0440	0.0612	2.56	
	0.0442	0.0615	2.55	
			Av. 2.54	2.55

gently tapping the instrument. Ethyl ether has the additional merit of rapidly evaporating, leaving a dry, clean apparatus and a dry specimen. Alcohol, benzene, and other liquids of low surface tension may be substituted for the use of the ether. The chief disadvantage of the use of ether lies in its extreme volatility but the errors incident to this property may be reduced to a minimum by proper attention to a few details of procedure. The use of ether permits the direct estimation of the density of most water-soluble salts.

Calibration of Instrument

The clean instrument is filled to slightly above an arbitrary lower mark with ether. The liquid is most conveniently introduced by means of a pipet. The device is allowed to stand until evaporation has reduced the level of the liquid to the exact mark on the capillary. Next ether is introduced from a weight buret till the liquid rises in the capillary to a second arbitrary mark. The marks on the author's instrument were 4.5 cm. apart. The buret is removed, quickly capped, and weighed. The loss in weight of ether is the calibration value for the particular temperature.

The calibration value is also to be determined with a lead clip in the instrument. This clip may subsequently be used to submerge specimens lighter than ether.

Method of Procedure

If the solid material is in the form of a powder, suitable fragments are selected for the determination with a forceps. In the case of a mineral the specimen is crushed and suitable fragments likewise selected. In the case of metals or alloys clippings or turnings may be used. Cut or massive gems require no sampling. Too fine powders are to be avoided since they give rise to errors from the inclusion of minute air voids between the individual particles of powder. Substances lighter than ether must be in a coherent mass so that a lead clip may be attached.

Table III—Estimation of Densities of Several Cut Gems

Sample	Displaced Ether Weight	Displaced Ether Volume	Density Found	Density Clerici's soln. (2)(6)
Grams	*Gram*	*Cc.*		
		SAPPHIRE		
0.4003	0.0710	0.0987	4.06	4.03
		TOPAZ		
0.5583	0.1121	0.1559	3.58	3.54
		LAZURITE		
2.5063	0.7479	0.1040	2 41	2 41
		RHODONITE		
2.0463	0.3945	0.5487	3.73	3.68

Table IV—Applicability of Method to Extreme Small Quantities of Various Substances

Sample	Displaced Ether Weight	Displaced Ether Volume	Density Found	Density Pycnometer
Gram	*Gram*	*Cc.*		
		POTASSIUM CHLORIDE		
0.0600	0.0216	0.0300	2.00	
	0.0218	0.0303	1.98	
	0.0218	0.0303	1.98	
			Av. 1.99	1.98
		SODIUM CHLORIDE		
0.0500	0.0166	0.0231	2.17	
	0.0159	0.0221	2.26	
	0.0162	0.0225	2.22	
			Av. 2.22	2.17
		COPPER WIRE		
0.0800	0.0064	0.0089	8.99	
	0.0065	0.0090	8.88	
	0.0066	0.0092	8.70	
			Av. 8.86	8.93
		CORK		
0.2098	0.6040	0.8401	0.25	0.24[a]

[a] Density of cork determined by chemical balance.

The sample being in readiness and weighed the instrument is filled with ether to the first mark by means of a pipet. The sample is quickly dropped in the instrument and the weight buret inserted. Ether is added from the buret till the liquid in the capillary rises to the second mark. The instrument is gently tapped to bring any air bubbles to the surface, and a final adjustment of levels is made. The buret is immediately removed, the stopper turned, the

buret capped, and weighed. The whole operation should be performed quickly. The loss in weight of the buret, subtracted from the calibration value, gives the weight of ether displaced by the specimen. Dividing the weight of displaced ether by its density of 0.719 gram per cubic centimeter gives the displaced volume of the specimen and a simple calculation serves to give the required density.

Temperature corrections for the expansion of the glass tube over the ordinary range of working temperatures is not required as it is less than the other errors involved.

Results

The results obtained on various substances are shown in Tables I to IV. The values by the pycnometer method were determined at 15° C. on large samples of the same material as used for the other determinations. The determinations by the ether method were done at approximately 15° C. Clerici's solution was used as a check in the case of the cut gems, the same gem being used in both determinations.

No difficulty was experienced in checking against the pycnometer in the case of the larger samples.

In the case of the cut gems the values do not check quite so closely but the ether method result is probably the one nearest to the actual value.

The individual determinations of the extremely small samples vary more from the true value than do those in which a larger volume of liquid is displaced, but the average value of a series is generally quite satisfactory.

The result with cork, noted on Table IV, shows that substances lighter than ether give concordant checks with the values obtained by other procedures.

The applicability of this method to large and small samples, and to substances lighter than the displacing liquid is very satisfactory. The procedure is rapid and the results obtained check with those obtained by other methods.

Literature Cited

(1) Caley, Ind. Eng. Chem., Anal. Ed., **2**, 177 (1930).
(2) Clerici, *Atti. accad. Lincei*, **16**, 187 (1907).
(3) Friedman and LaMer, Ind. Eng. Chem., Anal. Ed., **2**, 54 (1930).
(4) Kraus and Holden, "Gems and Gem Materials," p. 26, McGraw-Hill, 1925.
(5) Landes, *Am. Mineral.*, **15**, 159 (1930).
(6) Sullivan, Bur. Mines, *Tech. Paper* **381** (1927)
(7) Weinschenk and Clark, "Petrographic Methods," p. 179, McGraw-Hill, 1912.

Arc Spectrographic Estimation of Chromium in Ruby[1]

Jacob Papish and Wm. J. O'Leary

Department of Chemistry, Cornell University, Ithaca, N. Y.

The persistence of the arc spectral lines of chromium as conditioned by concentration of the element has been studied in the range between λλ 5785.8 and 3120.4 Å. The study was extended to chromium in a mixture of fused chromic oxide and alumina, and it was observed that the sensitivity of the spectral reaction was much greater in the case of chromium in fused alumina than in the case of chromium when arcked as chromic acid. The method was applied to the estimation of chromium in rubies.

Because synthetic rubies are colored red by the addition of from 2 to 4 per cent chromic oxide, it has been assumed that the color of natural rubies is also due to this substance. The presence of chromium in rubies has long been known (*2*); it is also known that there is not as much chromium in the natural gem as there is in the synthetic. According to Wöhler and Kraatz-Koschlau (*9*) the chromium in natural rubies is analytically not determinable, as it is present in very small amounts. Doelter (*1*) also states that the amount of chromium in natural rubies is so small that it cannot be determined quantitatively. Wild and Klemm (*8*) examined the emission spectra of rubies from Siam and Montana, using a carbon arc, and compared them with that of a synthetic ruby. They found that while all of them showed lines due to chromium, the synthetic ruby contained more chromium than natural ones, as evidenced by more intense lines. They report that the chromium lines λλ 3593.5 and 3578.7 Å. were missing in the spectrogram of the Siam ruby, and λ 2653.7 A. was missing in the spectrograms of the rubies from Siam and Montana.

In the present investigation, an arc spectrographic method was adopted to estimate the amount of chromium in naturally occurring rubies. The experimental procedure has been described elsewhere (*5*, *6*, *7*), and will be outlined only briefly here.

Persistence of Arc Spectral Lines of Chromium

A solution was prepared containing 1.923 grams of chromium trioxide in 100 cc. of aqueous solution. This was analyzed by titration with 0.1 *N* potassium permanganate and $FeSO_4.(NH_4)_2SO_4.6H_2O$ in the usual way and was found to contain 0.0099 gram of chromium per cubic centimeter. Because the error was only 1 per cent of the intended amount, and because the subsequent dilutions would make it still more negligible, the value 0.0099 gram was designated as 0.01 gram of chromium per cubic centimeter. This solution was diluted in volumetric flasks to give a series of solutions containing respectively, 0.01, 0.001, 0.0001, 0.00001, and 0.000001 gram of chromium per cubic centimeter. A one-tenth cubic centimeter sample of each of these solutions, measured from a calibrated capillary pipet, each sample containing, respectively, 1.0, 0.1, 0.01, 0.001, and 0.0001 milligram of chromium, was subjected to arc spectral excitation between graphite electrodes 7 mm. in diameter, on 110-volt direct current, using about 600 watts. The lower electrode was made the anode, and the samples were placed thereon. The spectrograph employed was of the Littrow auto-collimating type, fitted with a 30-degree quartz prism, and the spectra were photographed on d. c. ortho plates.[2]

Chromium yields a large number of arc lines in the optical spectral range that decrease in intensity and persistence with diminishing amounts of the element under excitation. The most sensitive of these lines between λλ 5785.5 and 3120.4 Å., with their persistence at varying concentrations, are listed in Table I. In this table, (v) is used to designate that a line is visible, (f) that it is faint, and (vf) that it is very faint. For the purpose of spectrographic estimation of small quantities the following lines were found most suitable: λλ 5208.4,

[1] Received August 22, 1930.

[2] Made by Eastman Kodak Company, Rochester, N. Y.

5206.0, 5204.6, 4626.2, 4622.5, 4619.5, 4616.1, 4613.3, 4546.0, 4544.6, 4540.7, 4535.7, 4530.7, 4289.7, 4274.8, 4254.3, 3605.3, 3593.5, and 3346.7 Å.

Table I—Persistence of Arc Spectral Lines of Chromium

λ	Milligrams of Chromium as CrO_3 1.0	0.1	0.01	0.001
5785.8				
5785.0				
5783.9				
5783.1	v			
5781.8				
5781.2				
5409.8	v			
5348.3	v	f		
5345.8	v	f		
5328.3	v	f		
5300.7	v	f		
5298.3				
5297.3	v	f		
5296.7				
5265.7	v	f		
5264.2	v	f		
5208.4	v	v	f	
5206.0	v	v	f	
5204.6	v	v	f	
4652.2	v	v	vf	
4646.2	v	v	vf	
4626.2	v	vf		
4622.5	v	vf		
4619.5	v	vf		
4616.1	v	vf		
4613.3	v	vf		
4546.0	v	vf		
4544.6	v	vf		
4540.7	v	vf		
4535.7	v	vf		
4530.7	v	vf		
4371.3	v	v		
4363.1	v	v		
4351.8	v	v		
4351.1				
4344.5	v	v		
4339.7	v	v		
4339.5				
4337.6	v	v		
4289.7	v	v	v	f
4274.8	v	v	v	f
4254.3	v	v	v	f
3976.7	v	v		
3969.8	v	f		
3963.7	v			
3941.5	v			
3928.7	v			
3921.0	v			
3919.2	v			
3916.3	v			
3908.8	v			
3894.1	v			
3743.9	vf			
3743.6				
3639.8	v	vf		
3636.6	v	vf		
3605.3	v	v	vf	
3593.5	v	v	vf	
3578.7	v	v		
3433.6	v	v		
3346.7	v	v	vf	
3132.1	v	v		
3120.4	v	v		

Arc Spectrographic Estimation of Chromium in Synthetic Rubies

In order to duplicate the conditions under which the natural rubies were to be examined, a number of synthetic rubies were prepared as follows:

An aqueous solution of ammonium chromium alum was prepared, containing approximately 0.01 gram of chromium per cubic centimeter. Definite portions of this solution (10, 5, and 0.5 cc.) were added to 44-gram portions of ammonium alum dissolved in water. The ammonium chromium alum solution was further diluted, and of this new solution, containing approximately 0.0001 gram of chromium per cubic centimeter, a 5-cc. and 0.5-cc. portion were added to 44-gram portions of ammonium alum dissolved in water. These amounts were calculated to yield rubies containing 2, 1, 0.1, 0.01, and 0.001 per cent chromium. The combined hydrous oxides of aluminum and chromium were then precipitated from each of the five mixtures by means of ammonium hydroxide, were filtered off, washed free of sulfate, and were ignited to aluminum oxide and chromic oxide. The hydrous oxides were precipitated together to ensure an intimate mixture with consequent uniformity of composition in the rubies.

Table II—Chromium Content of Synthetic Rubies

No.	Color	Chromium Determined %
1	Deep purplish red	1.84
2	Deep red	0.944
3	Pale pink	0.092
4	Very faint pink	0.009
5	White	0.0009

Table III—Persistance of Arc Spectral Lines of Chromium in Fused Alumina

λ	Milligrams of Chromium (as Cr_2O_3) in Fused Alumina 0.06	0.006	0.0006	0.00006
5785.8				
5785.0				
5783.9				
5783.1	v			
5781.8				
5781.2				
5409.8	v			
5348.3	v	f		
5345.8	v	f		
5328.3	v	f		
5300.7	v	f		
5298.3				
5297.3	v	f		
5296.7				
5265.7	v	f		
5264.2	v	f		
5208.4	v	v	f	
5206.0	v	v	f	
5204.6	v	v	f	
4652.2	v	v	vf	
4646.2	v	v	vf	
4626.2	v	vf		
4622.5	v	vf		
4619.5	v	vf		
4616.1	v	vf		
4613.3	v	vf		
4546.0	v	vf		
4544.6	v	vf		
4540.7	v	vf		
4535.7	v	vf		
4530.7	v	vf		
4371.3	v	v		
4363.1	v	v		
4351.8	v	v		
4351.1				
4344.5	v	v		
4339.7	v	v		
4339.5				
4337.6				
4289.7	v	v	v	f
4274.8	v	v	v	f
4254.3	v	v	v	f
3976.7	v	v		
3969.8	v			
3963.7	v	f		
3941.5	v			
3928.7	v			
3921.0	v			
3919.2	v			
3916.3	v			
3908.8	v			
3894.1	v			
3743.9	vf			
3743.6				
3639.8	v	vf		
3636.6	v	vf		
3605.3	v	v	vf	
3593.5	v	v	vf	
3578.7	v	v		
3433.6	v	v		
3346.7	v	v	vf	
3132.1	v	v		
3120.4	v	v		

Portions of each of the powdered mixed oxides were then put in a shallow graphite crucible, about 2.5 cm. in outside diameter, and the crucible was placed between the graphite electrodes of a horizontal arc furnace drawing 110 volts and approximately 300 amperes direct current. Separate crucibles were used for the different concentrations of chromium. The arc was then made to play on the sides of the crucible till the powdered oxides fused, this process usually requiring from 2 to 5 minutes. The resulting rubies were opaque, spherical in shape, and weighed 0.1 to 0.15 gram. Several grams of each of the different rubies were obtained in this way.

The color intensity of these rubies varied, as was to be expected, directly with their chromium content. The rubies were broken and examined microscopically; they were completely and homogeneously fused, were uniformly colored, and were crystalline aggregates, consisting of rhombohedra parallel to each other. This fact accounted in part for their opacity. They were then analyzed so as to determine the

actual amount of chromium present in them after possible losses by volatilization during the fusion. They were pulverized in a "diamond steel" mortar to pass a 200-mesh sieve, and were carefully gone over with a magnet to remove any particles of steel (*4*). Samples varying from 0.3 to 4.0 grams in weight were then fused in a platinum crucible with fifteen times their weight of potassium hydrogen sulfate. The fusions were taken up in nitric acid (1:2), oxidized with sodium bismuthate in the usual way (*3*), and titrated with 0.01 *N* potassium permanganate and $FeSO_4.(NH_4)\ SO_4.6H_2O$. The fusions in nearly all cases were complete the first time, but occasionally a small insoluble residue had to be re-fused with potassium acid sulfate before oxidation and titration. The results of these analyses are given in Table II.

The pulverized rubies were next examined spectrographically to determine the sensitivity and persistence of the chromium lines when alumina played the role of solvent. The powders were loaded onto the electrodes from a small hole bored in the end of a brass rod; from the average of a number of weighings, this hole was found to deliver a sample of ruby weighing 0.0063 gram. The sample was spread evenly over the lower electrode to ensure as complete volatilization as possible of all the material during the time of photographic exposure. The results of the observations are recorded in Table III.

A comparison of Table III with Table I will point out the fact that the sensitivity of the spectral reaction of chromium was much greater in the case of the synthetic rubies than in the case of chromium trioxide. The least recognizable quantity of chromium when introduced in the arc as chromic acid was 0.001 mg., but the same element in fused alumina was recognizable to the extent of 0.00006 mg.

Spectrographic Estimation of Chromium in Natural Rubies

Eight natural rubies from five different localities were subjected to arc excitation in the manner described in connection with the synthetic rubies. In each case about 6 mg. of pulverized ruby were used and the chromium was estimated from the number as well as from the intensity of spectral lines, by comparing the spectrograms with the "standards" used in compiling Table III. The results of this examination are recorded in Table IV.

Table IV—Spectrographic Estimation of Chromium in Natural Rubies

No.	Place of Origin	Description	Weight of Chromium (estd. in 6 mg. of ruby)	Estd. Chromium
			Mg.	%
1	Mysore, India	Dark red crystal, gem variety	0.006	0.1
2	Mysore, India	Red crystals, translucent	0.006	0.1
3	Macon County, N. C.	Pink, translucent	0.0006	0.01
4	Ural Mountains	Deep red crystals, translucent	0.006	0.1
5	Mysore, India	Deep red crystals, translucent	0.006	0.1
6	Zoutpansberg, Transvaal	Deep red crystal, opaque	0.006	0.1
7	Macon County, N. C.	Deep red crystal, translucent	0.002	0.03
8	Ceylon	Bright red, transparent	0.006	0.1

To check the reliability of the spectrographic method for estimating chromium in rubies, rubies Nos. 4 and 5, of which the writers had sufficient quantities, were examined by the procedure used for determining chromium in the synthetic rubies. The chromium content of ruby No. 4 was found to be 0.120 per cent, and of ruby No. 5, 0.159 per cent.

Literature Cited

(1) Doelter, *Sitzb. Akad. Wiss. Wien*, **117** [1], 819 (1908).
(2) Doelter and Leitmeier, "Handbuc h der Mineralchemie," Vol. 111, Pt. 2, p. 443, Leipzig, 1924.
(3) Mahin, "Quantitative Analysis," p. 467, New York, 1924.
(4) Moses, *Am. J. Sci.*, [4] **30**, 271 (1910).
(5) Papish, *Econ. Geol.*, **23**, 660 (1929).
(6) Papish, Brewer, and Holt, *J. Am. Chem. Soc.*, **49**, 3028 (1927).
(7) Papish and Holt, *Z. anorg. Chem.*, 192, 90 (1930).
(8) Wild and Klemm, *Centr. Mineral. Geol.*, **1926A**, 30.
(9) Wöhler and Kraatz-Koschlau, *Tschermak's mineral. petrog. Mitt.*, **18**, 456 (1899).

Elimination of Sulfur in Carbon Determinations by Direct Combustion[1]

Wm. H. Blatchley

4600 Jonathon St., Dearborn, Mich.

IN VIEW of the frequency of erroneous results in carbon determinations owing to the influence of sulfur, the discussions of the subject in the textbooks on steel analysis seem wholly inadequate, if not positively misleading.

A manufacturer of laboratory equipment has recently introduced a special carbon train designed for the elimination of sulfur. It involves the use of an electric heating unit and a catalytic cell for the conversion of sulfur dioxide to sulfur trioxide, followed by the usual zinc tower for its absorption.

The author of one of the well-known textbooks, in his latest edition, just off the press, recommends the use of red lead for all carbon determinations by combustion in steel, pig iron, and graphite, the context indicating that the object is to insure complete combustion of the carbon. In another paragraph he mentions the necessity, when dealing with materials containing an unusual amount of sulfur, of using an additional bubble tube or jar filled to a depth of 2 inches with a concentrated solution of potassium permanganate, to absorb "most of the unusual amount of sulfur dioxide which is formed."

In a series of experiments recently carried out by the writer, it was found that, under certain conditions, the sulfur can be effectively eliminated without recourse to any special additions to the conventional carbon train, even when igniting ferrous sulfide containing 27.4 per cent of sulfur.

The conditions under which this can be accomplished are as follows: The combustion tube is loosely packed in its outlet end with ignited asbestos which must extend into the hot part of the tube. After a few charges have been ignited in the tube with red lead flux, the asbestos becomes impregnated with a sublimate of this material. This is enough to oxidize to sulfur trioxide and fix in the form of lead sulfate the sulfur dioxide evolved by the average steel sample, whether a flux is used on the sample or not. If, then, red lead flux is used on pig irons and other high sulfur-bearing materials, the same reaction takes place in the combustion boat, and the effluent gases are free from sulfur dioxide.

[1] Received September 29, 1930.

Gravimetric and Direct Volumetric Determination of Cadmium[1]

R. C. Wiley

University of Maryland, College Park, Md.

Cadmium may be determined by precipitating as cadmium molybdate and weighing as such.

Cadmium may be determined volumetrically by titrating with a standard ammonium molybdate solution, using a saturated solution of pyrogallol in chloroform as an indicator.

CADMIUM is often determined gravimetrically by weighing the pyrophosphate or sulfate. It is commonly determined volumetrically by precipitating it as the sulfide, treating the sulfide with hydrochloric acid and then titrating with iodine solution. This of course is an indirect method.

Cadmium molybdate is very insoluble in a neutral solution. It is therefore possible to determine cadmium either by precipitating it as the molybdate and weighing it as such or by titrating a neutral solution of a cadmium salt with a standard molybdate solution. The end point of the titration may be determined by transferring some of the solution being titrated to a spot plate and bringing it into contact with a drop of chloroform saturated with pyrogallol. The solution tested must be nearly neutral. If the soluble molybdate is in excess, the aqueous drop which has been transferred will turn brown. Metals other than magnesium or the alkali metals will interfere with either method and must be removed.

Cadmium Solution Used in Determinations

A cadmium nitrate solution was prepared by dissolving 5.5150 grams of the metal in nitric acid, evaporating to dryness, and diluting to one liter. The cadmium in 25 cc. of this solution was determined as sulfate. No other metal was present.

The Gravimetric Method

The reagent ammonium molybdate is prepared by stirring up 30 grams of molybdenum trioxide with 400 cc. of water and a few drops of phenolphthalein and adding ammonia with constant stirring until the oxide is dissolved. Acetic acid is then added until the pink color disappears but the reaction is acid to litmus. After filtering, the solution is diluted to 1 liter. One cubic centimeter will precipitate 0.02 gram of cadmium.

Gooch crucibles should be prepared by covering the layer of ordinary asbestos with a layer of ground asbestos, and dried at 120° C.

Procedure for Gravimetric Method

The cadmium solution should be made just alkaline with ammonia and then just acid with acetic acid. It should then be heated to boiling and the molybdate solution added a drop at a time and with constant stirring. The presence of an excess may be determined by transferring a drop to the spot plate and testing with the pyrogallol indicator. The solution containing the precipitate is kept near the boiling temperature until the supernatant is clear or nearly so, and then allowed to stand for at least two hours and preferably overnight. It is then filtered through the Gooch, previously dried at 120° C. After the precipitate has been washed with warm water, the crucible containing it is dried at about 120° C., and weighed. The factor 0.4122 was used for converting cadmium molybdate to cadmium. The results are the following:

Cadmium present, 0.1378 gram
Cadmium found:
As sulfate, 0.1380, 0.1390, 0.1383, 0.1385; av. 0.1384 gram
Molybdate method, 0.1376, 0.1380, 0.1389, 0.1381, 0.1384, 0.1380, 0.1371, 0.1374; av. 0.1379 gram

These results show that the gravimetric molybdate is quite accurate.

In another solution there was present 0.2061 gram of cadmium and an average of four results shows 0.2062 gram present by molybdate method.

Discussion of Gravimetric Method

Cadmium molybdate as precipitated forms hard white crystals quite insoluble in water. It is, however, a little less soluble in a dilute solution of acetic acid than it is in water. Upon drying it assumes a faint pink tinge. It may readily be filtered and does not tend to clog the filter. The crystals are very small when first formed, resembling those of barium sulfate.

Too much suction should not be used in filtering, especially at the beginning, for the precipitate will tend to run through if it has not been digested long enough. This precipitate is readily washed. The use of ground asbestos in the Gooch is a precautionary measure.

Care should be used not to strike the sides or bottom of the beaker with the stirring rod when making the precipitation, since the crystals of cadmium molybdate will adhere tenaciously to the beaker at the point scratched and are detached only with great difficulty.

Cadmium molybdate is stable at 120° C. At about 500° C. it turns brown and loses about 3 per cent of its weight.

This compound is soluble in strong mineral acids and in concentrated solutions of bases. It is nearly insoluble in water, but soluble enough to give a very faint color with the pyrogallol indicator.

Volumetric Method

Prepare the standard as follows: Weigh out 7.4 grams of molybdenum trioxide, add about 100 cc. of water and some phenolphthalein. Dissolve in ammonium hydroxide and neutralize with acid. Cool and dilute to a liter with distilled water. The solution may be standardized by dissolving an exactly known amount of pure cadmium metal in nitric acid and evaporating to dryness over a water bath and then titrating the resulting cadmium nitrate against it, or it may be standardized by adding to a known volume of the solution an excess of cadmium salt and weighing the resulting cadmium molybdate as in the gravimetric method.

Procedure for Volumetric Method

The cadmium solution should be so treated that very little free acid is present. Ammonium hydroxide is then added until a precipitate begins to form. It is heated to boiling and the precipitate dissolved in the least possible amount of acetic acid. The solution is titrated and drops tested from time to time on a spot plate, the depressions of

[1] Received August 18, 1930.

which contain a saturated solution of pyrogallol in chloroform. At the end point a deep brown color will appear. The results are the following:

Cadmium present, 0.1378 gram
Cadmium found by volumetric method, 0.1390, 0.1380, 0.1395, 0.1374, 0.1378, 0.1390, 0.1386, 0.1390; av. 0.1385 gram

The above recorded results are only a few of those obtained and are given as typical. They show that cadmium may be accurately determined volumetrically.

Comment and Discussion

Ammonium salts increase the solubility of cadmium molybdate. They should be kept at a minimum. This increase in solubility due to ammonium salts is so small as to be negligible in the gravimetric method, but due to the great sensitiveness of the indicator it is appreciable in the volumetric method.

When the end point of the titration is apparently reached it should be boiled for about 30 seconds and retested, and if necessary more standard molybdate added.

Just before the end point is reached, a very faint yellow color may be noticed in the drop tested. This color is very faint and should not be confused with the much deeper color that appears when the true end point is reached.

A standard solution of ammonium molybdate appears to give a sharper end point than the sodium salt, although either may be used.

Potentiometric Determination of Saponification Number of Mixtures of Asphalt and Drying Oils[1]

James V. Demarest and Wm. Rieman, 3rd

School of Chemistry, Rutgers University, New Brunswick, N. J.

The saponification number of linseed oil can be determined potentiometrically without a blank determination and without the standardization of the alkali.

The saponification number of asphalt can be determined potentiometrically using anisole as a solvent.

Mixtures of linseed oil and asphalt can be analyzed by the potentiometric determination of the saponification number with high precision and with no more expenditure of time than is required in other methods.

The analysis of mixtures which contain soy bean oil or Bermudez asphalt is less satisfactory.

THE determination of the saponification number of mixtures of asphalt and drying oil is of considerable importance in the testing of asphalt paints. The standard method (*1*, *2*), however, is rather difficult and inaccurate because the black color of the asphalt suspension obscures the end point of the indicator. Furthermore, when the benzene is evaporated, the asphalt is precipitated and considerable alkali is occluded by the asphalt. The method described in this paper overcomes the first difficulty by the use of the hydrogen electrode and the second difficulty by the use of anisole as a solvent.

Method

The application of the hydrogen electrode to the determination of the saponification number of the gilsonite was investigated first. To a weighed sample of gilsonite were added 50 cc. of standard alcoholic potassium hydroxide (about 0.7 *N*) and 40 cc. of pure anisole. The mixture was refluxed until saponification was complete (1 hour). After cooling it was titrated potentiometrically with standard aqueous hydrochloric acid. A normal calomel electrode and a hydrogen electrode of the usual type were used as reference and indicator electrodes, respectively. After each titration the hydrogen electrode was treated with hot concentrated nitric acid and then made the cathode in the electrolysis of dilute sulfuric acid. After this treatment it was ready for the next titration. It was found unnecessary to replatinize an electrode during the entire investigation. A Leeds and Northrup student potentiometer was used.

Anisole was found to be the best solvent for this purpose. Other asphalt solvents such as ethyl ether, propyl ether, and isopropyl ether were unsatisfactory because they failed to keep a major portion of the asphalt in solution. Nujol was unsatisfactory because it formed a thick emulsion when hydrogen was bubbled through saponified mixtures of linseed oil and asphalt. The benzene could not be used because it poisoned the hydrogen electrode. During the titration two layers separated, the upper anisole layer containing almost all of the asphalt. About 9 minutes were required to attain a steady potential after each addition of acid.

The differential curve of a typical titration is shown in Figure 1. The first maximum represents the neutralization of excess alkali. The reason for the existence of the second maximum is not clear, but may be due to the existence of acids in the gilsonite of very different ionization constants. The third maximum occurs at the same volume of acid as is required to neutralize 50 cc. of the alcholic alkali, and therefore represents the completion of the reaction between hydrochloric acid and the alkali combined with the asphalt. In this determination it is unnecessary to standardize the alkali because the amount of acid used between the first and last maxima is a direct measure of the combined alkali. The results are given in Table I.

Table I—Saponification Number of Asphalts

Gilsonite		Bermudez
Blank method	Double maximum method	Blank method
11.2	12.3	26.9
9.1	8.6	28.0
9.3	8.5	27.7
10.0	...	....
Mean 9.9	9.8	27.5

Next a sample of linseed oil was saponified and titrated by exactly the same method, including the addition of the anisole. In this case only 5 minutes were required to attain a steady potential. A representative curve is given in Figure 2. Here only two maxima are found. The first

[1] Received August 28, 1930. From a thesis submitted to the faculty of Rutgers University by James V. Demarest in partial fulfilment of the requirements for the degree of master of science.

256692

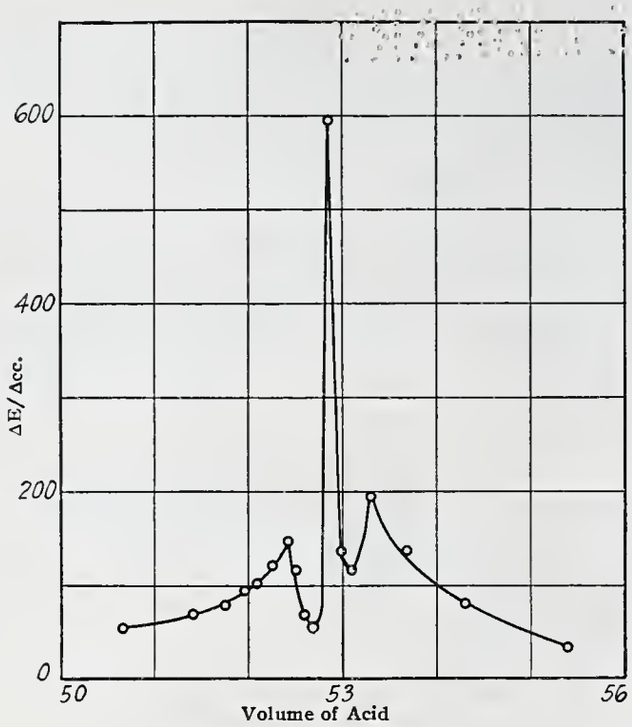


Figure 1—Gilsonite

represents neutralization of excess alkali; the second, the complete displacement of fatty acids from the soaps. The results are given in Table II.

Table II—Saponification Number of Linseed Oil

Indicator Method	Potentiometric Methods	
	Blank	Double maximum
191.1	192.3	192.9
191.6	192.7	194.0
190.9	193.2	191.9
192.6	192.6	...
193.1	193.1	...
192.4	192.5	...
191.5	192.4	...
191.4	192.7	...
191.6		
Mean 191.8	192.7	192.9

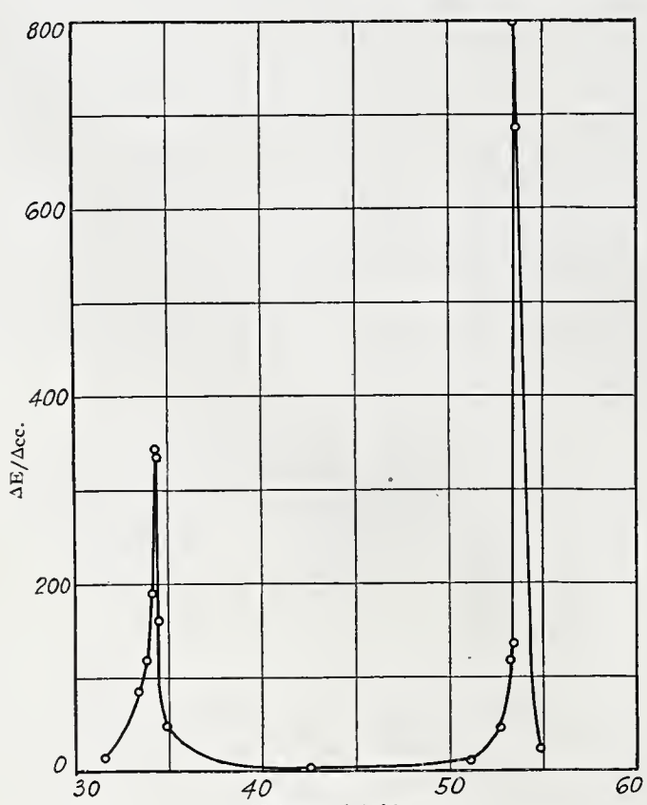


Figure 2—Linseed Oil

The saponification number of soy bean oil was determined potentiometrically in the presence of anisole, and found to be 198.0.

Mixtures of known quantities of linseed oil and gilsonite were then prepared and these mixtures were analyzed by a potentiometric determination of the saponification number. The data and curve of a typical titration are given in Table III and Figure 3.

Table III—Titration Data for Linseed Oil and Gilsonite

Cc.	*E, volts*	*ΔE/Δcc.*	*Cc.*
40.12	1.0145	...	...
41.12	0.9710	43	40.62
41.42	0.9230	160	41.28
41.52	0.9045	185	41.48
41.62	0.8870	175	41.57
41.72	0.8715	155	41.67
41.82	0.8575	140	41.77
42.13	0.8195	123	41.98
52.66	0.6790	13	47.39
52.96	0.6710	27	52.81
53.06	0.6675	35	53.01
53.16	0.6640	35	53.11
53.26	0.6570	70	53.21
53.36	0.6440	130	53.31
53.46	0.6330	110	53.41
53.56	0.5610	720	53.51
53.66	0.5150	460	53.61
54.16	0.4430	144	53.91
56.16	0.4040	19	55.16

Again only two distinct maxima are found which represent the neutralization of free and combined alkali, respectively. The results are given in Table IV.

Table IV—Analysis of Mixtures

True Composition		Oil Found	
Gilsonite	Linseed oil	Blank method	Double maximum method
%	%	%	%
19.8	80.2	80.1	....
19.7	80.3	81.0	80.3
36.9	63.1	62.7	63.1
57.2	42.8	43.3	42.9
58.2	41.8	42.3	41.9
78.3	21.7	20.5	21.0
	Soy bean oil		
59.9	40.1	42.8	
58.7	41.3	42.4	
59.6	40.4	41.7	
Bermudez			
64.8	35.2	40.4	
61.6	38.4	44.4	
62.1	37.9	43.1	

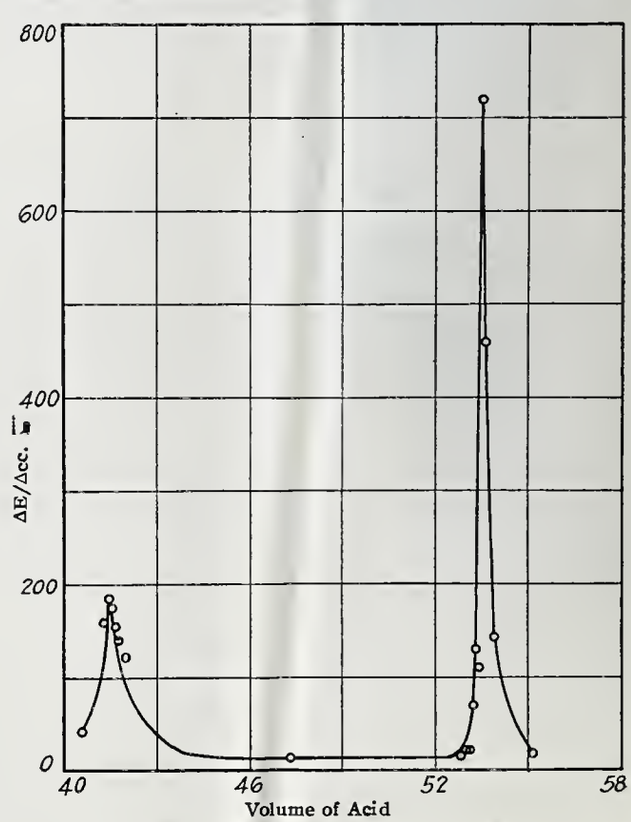


Figure 3—Linseed Oil and Gilsonite

The method was applied to mixtures of soy bean oil with gilsonite and with Bermudez asphalt with less success. Difficulty was experienced in detecting the last maximum. It is recommended, therefore, that standard alcoholic base be used in the analysis of mixtures which contain soy bean oil. These results are also given in Table IV.

Literature Cited

(1) Abraham, "Asphalt and Allied Substances," Van Nostrand, 1918.
(2) Marcusson, *Chem.-Ztg.*, **36**, 803 (1912).

Effect of Amino Acids upon Rotation of Glucose and Fructose and Its Significance to Determination of Sucrose by Double Polarization Methods[1]

D. T. Englis and F. A. Dykins

Chemical Laboratory, University of Illinois, Urbana, Ill.

The effect of increase in alkalinity upon the combination of glucose with glycine, as previously noted by Euler and associates, has been extended with studies of the effect of temperature and different molar relationships. The extent of combination has been followed polarimetrically and by an iodometric determination of uncombined glucose.

The increase in combination with increase in pH, and the equilibrium constants for the reaction as determined by polarimetric and iodometric methods, were in agreement with each other and with results obtained by Euler from freezing point data.

At 25° C. the glycine-glucose complex was almost completely reversed by acidification while at a temperature as low as 35° C. some of the stable type of melanoidal combination, not affected by acid, was evident. Near 0° C. the extent of the reaction was very limited.

Similar experiments were carried out with asparagin and glucose and the same general effects noted although the two methods gave values of different magnitudes.

Fructose showed no optical changes in the presence of glycine and asparagin with increasing pH which could not be attributed to alkalinity alone.

The significance of the effect of pH, time of standing, and temperature upon the determination of sucrose in the presence of amino acids by double polarization method is discussed.

THE importance of more exact knowledge of the effect of certain optically active nitrogenous impurities upon simple sugars and its significance to the determination of sucrose by the double polarization method is evident from the recent referee studies reported upon this subject by Zerban (*15*, *16*).

The information is especially necessary in studies of carbohydrate metabolism of plants in which the sugar concentration is quite low and the concentration of the nitrogenous materials relatively higher in proportion to the sugars than in the juice of plants used as sugar sources. Brown and Morris (*2*), who are perhaps among the earliest workers to make a detailed study of the individual carbohydrates in plants, call attention to a disparity between the value for sucrose determined by polarization as compared to chemical methods. The magnitude of the difference varied with different plant materials and with different portions of the same plant. More recently Davis and co-workers, in estimating the carbohydrates of the mangold and potato, found polarization values as much as 80 per cent greater than the reduction values and sometimes as much as 90 per cent lower. The variation was generally greatest in the stem extracts. Davis (*5*) has made the assumption that the fluctuations between the optical and chemical values is due to asparagin and glutamin. In this laboratory, in the investigation of the effect of potassium salts upon the carbohydrate metabolism of the nasturtium, the results of the determination of sucrose by polarimetric methods have been consistently higher. This has led to a series of studies in an effort to determine the causes of the differences, and to find a means of eliminating the more serious sources of error.

[1] Received September 4, 1930.

Somers (*14*) investigated first the effect of reduction due to sucrose upon the chemical method; second, the effect of certain salts left after different defecation procedures; and finally, the influence of asparagin upon the optical values. These factors taken separately were found to have comparatively little effect, but some observations of the last mentioned are of special interest.

An asparagin solution and invert solution were prepared and portions of each were mixed with an equal volume of water. Then equal portions of each original solution were mixed together. The mixture showed an increased levorotation over the sum of the optical values of the individual constituents.

A few years later, Drake (*6*) studied the effect of the presence of a large number of amino acids upon glucose, fructose, and sucrose before and after its inversion. An effort was made to keep the solutions approximately neutral to avoid the effect of change in acidity upon the rotation of the amino acid itself. Both plus and minus differences in rotation of the mixtures were found but the value of the work suffers from lack of exact knowledge of the acidity and duration of the reaction period.

In 1925, Nueberg and Kobel (*11*) made observations of a somewhat similar character. These investigators were concerned with a probable reaction product between sugar and amino acid which accelerated the alcoholic fermentation of the sugar. Addition of *d-l*-alanine to a fructose solution increased the levorotation while with glucose very little effect was noted. Supplementary work by Neuberg and Kobel (*12*) indicated that fructose seems to react immediately with amino acids and amides at a pH of 7. Particularly striking increases in levorotation were given by aspartic

and glutamic acids. With the aldol sugars the effects were much less.

It has been pointed out by Browne (*3*) and others whom he quotes that optical rotation in the ordinary sense of the term is not an additive property. It follows as a consequence that a discrepancy between the rotation of a mixture and the sum of the rotations of its constituents does not necessarily mean that a reaction has taken place between the constituents. Although the effect of the water concentration which Browne has emphasized would probably not be sufficient to account for the total differences observed by Somers and other investigators cited, additional indications of a reaction should be furnished by other methods. This has been done by Euler and his associates.

Euler and Josephson (*10*) gave attention to the effect of decreasing hydrogen-ion concentration upon the reaction of glucose with glycine. At the isoelectric point of glycine no reaction took place, but with increasing pH, the apparent combination as indicated by change in polarization was 32 per cent at a pH of 9.6. A more detailed study by Euler and Brunius (*7*, *8*, *9*) in which the reaction was followed by freezing point lowering, determination of uncombined amino acid by the Van Slyke method and glucose by the iodometric method, in addition to polarimetric change, confirmed the earlier observations. It was observed that the rate of combination of glucose with glycine is slow, but at a pH of 9.5, based on observations of freezing point lowering, it reaches equilibrium at 53 per cent combination in 48 hours. Glucose and alanine behaved in a similar fashion. The first explanation advanced for the increase in extent of reaction with increase in pH was that the alkalinity favored the change of the sugar from the lactone to the free aldehyde form which then condensed with the amino group. Preliminary treatment of the sugar with alkali had no effect on the final reaction, so any previous rearrangement to the acyclic form did not accelerate the combination. Additional evidence from refractometric observations seemed to indicate absence of a double-bonded compound, and it was concluded that the union between sugar and amino acid was of glucosidal character.

While the experiments of Neuberg and Kobel, and Euler and his associates were carried out with a biological application in view, they are not less important from the standpoint of analysis.

In the present study some of the previously reported experiments with glycine have been extended and additional experiments carried out with asparagin, a representative of one of the more common nitrogenous impurities in plant extracts.

Experimental Methods

The amino acids and sugars had been carefully purified and were of high quality. Glycine was selected as one of the amino acids for study since it is optically inactive and hence the complications due to the change in rotating power of the acid itself are eliminated.

Sodium hydroxide was added to the amino acid solution to bring it to a definite pH and then the solution made to volume with a carbonate-bicarbonate buffer. The sugar solution was similarly buffered. Amino acid and sugar solutions were then mixed in equal quantities, and for the purpose of control an equal volume of each was mixed with an equal volume of buffer solution. The hydrogen-ion concentration of each of the prepared solutions was measured. A Leeds and Northrup potentiometer was used with a Hildebrand hydrogen electrode and a 0.1 *N* calomel half-cell. The e. m. f. of the solution was measured and the pH calculated. An atmosphere of purified hydrogen was maintained above the solution to insure a steady potential. The reactions were allowed to proceed at various pH values and various temperatures until equilibrium was reached. In most of the experiments the concentrations of the mixture were in a 1 to 1 molecular ratio. In others the amino acid was reduced, keeping the molar concentration of glucose constant. In all experiments the extent of the reaction was determined by decrease in optical value. The observations were made with a Schmidt and Haensch saccharimeter. In some of the mixtures the uncombined sugar was determined by a slight modification of the Cajori (*4*) iodometric method for aldol sugars, and the uncombined amino acid estimated by the Van Slyke (*13*) method.

Calculations of equilibrium constants, glucose-amino complex ÷ glucose × amino acid, were made on the assumption that the combination is in an equal molecular ratio and that the compound formed is of negligible rotation so that the decrease in rotation is equivalent to the extent of combination. This assumption will be open to criticism. Euler has made a calculation of the probable optical activity of compound and found it to be comparatively high. However, if one accepts the theory of a glucosidal structure and if the amino acid reacts equally well with the α and β forms of glucose, one would anticipate that little change in rotation would occur if the glycine glucosides differ in rotation from their respective forms of glucose as do the methyl glucosides.

The detailed results of these experiments are given in Table I.

Table I—Effect of Glycine on Glucose at Various pH Values

Part I—Optical Changes (2 dm. tube)

Temperature, 25° C.; molar concentration, 0.0666

pH	Time	Glucose 50 cc. Glycine 50 cc.	Decrease in Rotation		Equilibrium Constant
	Hrs.	° *V.*	° *V.*	%	
8.11	0	3.60	0.00	0.00	
	24	3.53	0.07	1.94	
	48	3.50	0.10	2.77	0.43
9.52	0	3.60	0.00	0.00	
	24	3.12	0.48	13.33	
	48	3.00	0.60	16.66	3.5
10.30	0	3.60	0.00	0.00	
	7	3.51	0.09	2.50	
	19	3.14	0.46	12.77	
	26	3.03	0.57	15.83	
	42	2.94	0.66	18.33	
	48	2.80	0.80	22.22	5.5

Part II—Decrease in Apparent Glucose by Iodometric Method

Glucose-Glycine Mixture	pH	0.1116 *N* I_2 Soln.	Glucose Present	Glucose not Accounted for	Loss of Glucose
Cc.		*Cc.*	*Mg.*	*Mg.*	%
10	8.11	11.57	116.56	3.44	2.87
10	9.52	10.18	102.20	17.80	14.83
10	10.30	9.26	92.97	27.03	22.53

Part III—Uncombined Amino Acid by Van Slyke Method

Temperature, 26° C.; barometer, 749 mm. Hg

Glucose-Glycine Mixture	pH	N_2 Formed	Glycine in Sample	Total Glycine Found in Mixture (1.000 Gram Present)
Cc.		*Cc.*	*Mg.*	
10	8.11	16.64	50.10	1.002
10	9.52	16.49	49.65	0.993
10	10.30	16.56	49.86	0.997

Part IV—Summary of Results

pH	Apparent Combined Glucose		Apparent Combined Glycine
	Polarimetric	Iodometric	Van Slyke method
	%	%	%
8.11	2.77	2.87	0.0
9.52	16.66	14.83	0.9
10.30	22.22	22.53	0.5

Experiments with Asparagin

A series of experiments analogous to those with glycine were carried out with asparagin and the results are recorded in Table II.

Table II—Effect of Asparagin on Glucose at Various pH Values

Part I—Optical Changes (2 dm. tube)

Temperature, 25° C.; molar concentration, 0.0666

pH	Time	Glycine 50 cc. Glucose 50 cc.	Decrease in Rotation	
	Hrs.	° *V.*	° *V.*	%
8.75	0	3.65	0.00	...
	24	3.50	0.15	4.11
	48	3.50	0.15	4.11
	72	3.50	0.15	4.11
10.64	0	3.65	0.00	...
	24	3.20	0.45	12.33
	48	2.71	0.94	25.75
	72	2.67	0.98	26.85
11.55	0	3.65	0.00	...
	24	1.35	2.30	63.01
	48	0.41	3.24	88.76
	72	0.23	3.42	93.72

Part II—Decrease in Apparent Glucose by Iodometric Method

Glucose-Asparagin Mixture	pH	0.1116 *N* I_2 Soln.	Glucose Present	Glucose not Accounted for	Loss of Glucose
Cc.		*Cc.*	*Mg.*	*Mg.*	%
10	8.75	11.97	120.10	...	...
10	10.64	10.70	107.40	12.60	10.50
10	11.55	7.26	72.89	47.11	39.26

Part III—Uncombined Amino Acid by Van Slyke Method

Temperature, 26° C.; barometer, 749 mm. Hg

Glucose-Asparagin Mixture	pH	N_2 Formed	Asparagin in Sample	Total Asparagin in Mixture = 0.440 gm.
Cc.		*Cc.*	*Mg.*	*Gm.*
10	8.75	4.16	22.04	0.441
10	10.64	4.07	21.57	0.431
10	11.55	4.10	21.73	0.434

Part IV—Summary of Results

pH	Apparent Combined Glucose		Apparent Combined Glycine
	Polarimetric	Iodometric	Van Slyke method
	%	%	%
8.75	4.11	0.00	0.0
10.64	26.85	10.50	2.04
11.55	93.72	39.26	1.36

Effect of Acidification on the Reversibility of the Reaction

Euler and Brunius (*8*) found that, when solutions of alanine and glucose with a pH of 10.4 had been allowed to stand until equilibrium was reached and then acidified with sulfuric acid, after 25 hours the iodine consumption was almost the same as the initial value, indicating a reversibility of the reaction. Such reversibility should characterize all glucose-amino compounds. To demonstrate this point solutions were prepared in double the concentration indicated in Table I, Part I, and polarized. They were allowed to stand 48 hours, polarized, and acidified with an equal volume of dilute hydrochloric acid. After 48 hours the solutions were again polarized. The results are given in Table III.

Table III—Effect of Acidification upon Glucose-Amino Acid Condensation Product

Molar concentration, 0.1332

pH	Glucose 50 cc. Glycine 50 cc.	After 48 Hours	Add Equal Volume Dil. HCl	After 48 Hours
	° *V.*	° *V.*	° *V.*	° *V.*
8.11	7.20	7.00	3.50	3.60
9.52	7.20	6.30	3.15	3.50
10.30	7.20	5.60	2.80	3.40

Effect of Variation in Glucose-Glycine Ratio upon Their Combination

The next experiments were designed to determine the effect of altering the ratio of the glucose and glycine upon the optical value at different pH values. The majority of sugar juices or sirups contain sugar in large excess of the amino acids so that the mass action effect of the sugar is quite high, and one would expect almost all the amino acid to be in combination. In this study the glucose concentration was kept constant, and that of the glycine reduced. The general method of procedure was the same as previously outlined. After equilibrium was reached, solid oxalic acid was added, and the rate of reversion to the original constituents followed. These experiments were carried out at room temperature during an exceedingly warm summer and the thermometer registered close to 35° C. during the whole period. The results are given in Table IV.

Table IV—Effect of Changes in Glucose-Glycine Ratio and pH upon Rate of Change in Optical Value of Solution. Rate of Change on Acidification

Part I—Original pH, 9.52; Temperature, 35° C.; Molar Concentration of Glucose, 0.222

Reaction Period	Rotations: Initial glucose-glycine ratio				Apparent Combination: Initial glucose-glycine ratio			
	1:1	1:0.5	1:0.25	1:0.125	1:1	1:0.5	1:0.25	1:0.125
Hrs.	° *V.*	° *V.*	° *V.*	° *V.*	%	%	%	%
0	12.24	12.24	12.24	12.24	0.0	0.0	0.0	0.0
6	9.66	10.85	11.39	11.84	21.0	22.7	27.7	26.2
18	8.39	10.35	11.17	11.56	31.4	30.9	35.0	44.4
24	8.12	10.16	10.86	11.55	33.7	33.9	45.1	45.1
30	8.32	9.93	10.77	11.55	32.0	37.7	48.0	45.1
42	8.04	9.83	10.78	11.28	34.3	39.3	47.7	62.7
48	8.12	9.93	10.89	11.44	33.7	37.7	44.1	52.3
After addition of solid oxalic acid								
0	8.12	9.93	10.89	11.44	33.7	37.7	44.1	52.3
6	10.97	11.35	11.43	11.60	10.3	14.5	26.4	41.8
18	11.18	11.23	11.38	11.53	8.7	16.5	28.1	46.4
66	11.06	11.57	11.39	11.66	9.6	10.9	27.7	37.9
(A) Per cent reduction of rotation due to destruction of glucose or formation of a non-dissociable compound.					9.6	10.9	27.7	37.9
(B) Per cent combined at equilibrium after correction for (A).					24.1	26.8	16.4	15.5

Part II—Original pH, 10.3; Temperature, 35° C.; Molar Concentration of Glucose, 0.222

Reaction Period	Rotations: Initial glucose-glycine ratio				Apparent Combination: Initial glucose-glycine ratio			
	1:1	1:0.5	1:0.25	1:0.125	1:1	1:0.5	1:0.25	1:0.125
Hrs.	° *V.*	° *V.*	° *V.*	° *V.*	%	%	%	%
0	12.24	12.24	12.24	12.24	0.0	0.0	0.0	0.0
6	9.50	10.63	11.35	11.80	22.4	26.3	29.0	28.9
18	8.10	10.38	10.98	11.28	33.8	30.4	41.2	62.7
24	7.89	9.63	10.70	11.16	35.5	42.6	50.3	70.6
30	7.85	9.63	10.56	11.00	35.8	42.6	54.9	81.0
42	7.77	9.65	10.60	11.07	36.5	42.3	53.6	76.4
48	7.82	9.63	10.51	11.03	36.1	42.6	56.6	79.1
After addition of solid oxalic acid								
0	7.82	9.63	10.51	11.03	36.1	42.6	56.6	79.1
6	11.01	11.21	11.07	11.03	10.0	16.8	38.2	79.1
18	11.01	11.03	11.10	10.86	10.0	19.8	37.2	90.2
66	10.93	11.21	11.00	10.89	10.7	16.8	40.5	88.2
(A) Per cent reduction of rotation due to destruction of glucose or formation of a non-dissociable compound.					10.7	16.8	40.5	88.2
(B) Per cent combined at equilibrium after correction for (A).					25.4	25.8	16.1	..

Method of Calculations

Calculation of the apparent percentage of glycine in combination may be indicated as follows: In Table IV, Part II, the ratio of glucose to glycine is 1 to 0.5. The decrease in rotation indicates an apparent loss of glucose equal to 21.3 per cent. Since one mol of glycine combines with one mol of glucose and its initial concentration is only half that

of the glucose, then 42.6 per cent of it may be considered as in combination.

The equilibrium values at 48 hours would seem to indicate that as the glucose is increased in proportion to glycine, a greater percentage of glycine is brought into combination. However, when the solutions are acidified, they fall far short of returning to their original values. Apparently, at this higher pH and temperature the type of melanoid reaction recently discussed by Ambler (*1*) begins to take place between sugar and amino compound. In addition there may be some alteration of the glucose itself. Consequently calculations of even apparent equilibrium constants are out of the question.

Effect of Temperatures of 0° C. and 50° C. upon Reaction of Glucose and Glycine at pH 10.3

The temperature of 35° C. having given a non-dissociable compound of sugar and amino acid, a couple of experiments were carried out to determine the effect of a greater range from ordinary room temperatures. The glycine and glucose were again used in equivalent amounts, and the solutions buffered at a pH of 10.3. Blanks containing sugar and buffer alone were examined at the same time. Experiments were run in duplicate, one series of flasks being placed in a refrigerator at 0° C., and the other in an oven at 50° C. The observations of rotation are given in Table V.

Table V—Effect of Different Temperatures upon Reaction of Glucose and Glycine at a pH of 10.3

Part I—Temperature, 0° C.; Molar Concentration, 0.222

Reaction Period	Control: Glucose and Buffer				Glucose-Glycine and Buffer			
	Rotation (*a*)	Rotation (*b*)	Change (*a*)	Change (*b*)	Rotation (*a*)	Rotation (*b*)	Change (*a*)	Change (*b*)
Hrs.	° *V.*	° *V.*	%	%	° *V.*	° *V.*	%	%
0	12.24	12.24	0.0	0.0	12.24	12.24	0.0	0.0
12	12.20	12.18	0.3	0.4	11.80	11.78	3.5	3.7
24	12.16	12.16	0.6	0.6	11.80	11.78	3.5	3.7
36[a]	12.02	12.02	1.6	1.6	11.76	11.76	3.9	3.9
72	12.00	12.00	1.8	1.8	11.76	11.76	3.9	3.9

Part II—Temperature, 50° C.; Molar Concentration, 0.222

Reaction Period	Control: Glucose and Buffer				Glucose-Glycine and Buffer			
	Rotation (*a*)	Rotation (*b*)	Change (*a*)	Change (*b*)	Rotation (*a*)	Rotation (*b*)	Change (*a*)	Change (*b*)
Hrs.	° *V.*	° *V.*	%	%	° *V.*	° *V.*	%	%
0	12.24	12.24	0.0	0.0	12.24	12.24	0.0	0.0
3	9.44	9.88	22.9	19.3	8.14	8.42	33.5	31.2
6	8.38	8.50	31.5	30.5	7.76	7.78	36.6	36.4
12	7.22	7.22	41.0	41.0	6.98	7.02	42.9	42.6
24	6.46	6.54	47.2	46.5	6.02	6.02	50.8	50.8
36	6.52	6.52	46.7	46.7	Dark	Dark	..	..

[a] At end of 36-hour period the temperature had risen somewhat due to trouble with mechanical refrigerator. Experiments were continued in an ice chest a few degrees above zero.

At the lower temperatures, the solutions remained perfectly clear and uncolored throughout the experiment. Even at relatively high pH values, the amino acid and sugar react to a very limited extent and the equilibrium value at the low temperature is practically reached within the first 12 hours.

At the higher temperature, both the control and the mixture became dark colored, but the mixture was very much darker than the control containing no amino acid. Addition of oxalic acid caused but little change in rotation, indicating that the products of the reaction were of a very stable character.

Effect of Amino Acids on Fructose at Various pH Values

Neuberg and Kobel (*12*) have demonstrated that at a pH of 7, fructose tends to react immediately with amino acids to give products of a lower rotatory value. It seemed desirable to determine the effect of increasing alkalinity upon such sugar mixtures. Accordingly experiments were tried with glycine and asparagin. The results are given in Table VI.

Table VI—Effect of Glycine and Asparagin upon Optical Value of Fructose at Various pH Values

Temperature, 25° C.; molar concentration, 0.222

pH	Time	Rotation (4-dm. Tube)		
		Levulose and buffer	Levulose-glycine	Levulose-asparagin
	Hrs.	° *V.*	° *V.*	° *V.*
8.15	0	−19.69	−19.61	−19.87
	79	−19.55	−19.52	−19.78
9.52	0	−19.48	−19.54	−19.79
	79	−19.44	−19.50	−19.82
10.30	0	−19.41	−19.46	−19.74
	79	−19.42	−19.44	−19.72

Discussion of Results

As can be noted in Table I, and in agreement with observations of previous workers, the effect of decreasing the hydrogen-ion concentration is to increase the tendency of the sugar and amino acid to react, and the rate of reaction is fairly slow. The very satisfactory agreement between the values for the extent of combination of glucose and glycine, as determined by polarimetric and iodometric methods, and the almost complete recovery of amino acid when the mixture is analyzed by the Van Slyke method, are, however, somewhat at variance with the results of Euler and his associates for the same pH values. It should be pointed out that their mixtures of glycine and glucose were in the ratio of 2 mols of the former to 1 of the latter, and their iodometric method necessitated a much more strongly basic solution. The difference in the Van Slyke values may be attributed to a longer period of time consumed in the analyses here reported, with the result that under these conditions the amino-acid sugar complexes had almost completely reverted to the original constituents.

The equilibrium constants, as calculated, lie close to the curve which Euler and Brunius (*7*) obtained by the freezing point method for the extent of combination at different pH values. This fact, in addition to the agreement between the polarimetric and iodometric values of Table I, Part IV, lends support to the assumption that the glucose-glycine compound is of negligible optical activity.

A complete dissociation of the glucose-glycine complex is evident after acidification of the solutions of low alkalinity, but in the solutions of higher alkalinity there appears to be either a slight destruction of glucose or the formation of some non-dissociable product.

The results with asparagin are similar except that an enormous change in optical value takes place which is probably due to the effect of the alkali upon the amino acid itself in addition to the favoring of the condensation reaction.

As can be noted in Table VI there is little change in increasing alkalinity upon the keto sugar-amino acid complex. Any differences observed are probably due to the effect of the alkaline solution upon the sugar itself.

Significance of Effect of Amino Acids upon Determination of Sucrose by Double Polarization Methods

The effects of change in the optical value of the amino acids and fructose with change in acidity of the solution, hydrolysis of reversion products, and chemical change in some of the amino acids themselves, upon the determination of sucrose by the double polarization method with different hydrolytic procedures, have been discussed by Zerban (*15*, *16*). However, he states that a preliminary study of the methods following lead clarification gave such divergent results by

two chemists working in the same laboratory that work along this line was postponed temporarily.

Since raw sugar solutions are usually defecated with lead acetate and the excess lead removed with sodium carbonate or a similar reagent before the determination of sucrose, the pH of the solution may be very markedly increased by both the excess of deleading agent and the soluble acetate salt produced in the lead precipitation process. This may be expected to favor the amino acid–aldol sugar combination, the extent depending on the relative quantities of each present, the alkalinity of the solution, and the time the solutions are allowed to stand before polarizing. Even if acid be added to bring to some definite pH near the neutral point, the rate of reversion of the complex to its original components in low acid concentration is slow and the time required to reach an equilibrium value may be several hours. In addition, the temperature of the solution exerts a marked influence upon the extent and nature of the complex formed. Thus the apparent change due to the hydrolysis of the sucrose can vary widely and be either higher or lower than the theoretical value. The variations between polarimetric and reduction previously mentioned as observed by Brown and Morris, Davis, and others probably result from all those factors.

It is evident that satisfactory results for sucrose by the double polarization method must involve very careful consideration of this tendency of amino acids and glucose to combine as well as the many other factors which have received attention previously.

Literature Cited

(1) Ambler, Ind. Eng. Chem., **21**, 47 (1929).
(2) Brown and Morris, *J. Chem. Soc.*, **63**, 664 (1893).
(3) Browne, *Louisiana Planter*, **67**, 44 (1921).
(4) Cajori, *J. Biol. Chem.*, **54**, 617 (1922).
(5) Davis, *J. Agr. Sci.*, **7**, 327 (1916–17).
(6) Drake, B.S. Thesis, University of Illinois, 1924.
(7) Euler and Brunius, *Ber.*, **59B**, 1581 (1926).
(8) Euler and Brunius, *Z. physiol. Chem.*, **155**, 259 (1926).
(9) Euler and Brunius, *Ibid.*, **161**, 265 (1926).
(10) Euler and Josephson, *Ibid.*, **153**, 1 (1926).
(11) Neuberg and Kobel, *Biochem. Z.*, **162**, 496 (1925).
(12) Neuberg and Kobel, *Z. physiol. Chem.*, **174**, 464 (1926).
(13) Slyke, Van, *J. Biol. Chem.*, **9**, 185 (1911).
(14) Somers, B.S. Thesis, University of Illinois, 1920.
(15) Zerban, *J. Assoc. Official Agr. Chem.*, **11**, 175 (1928).
(16) Zerban, *Ibid.*, **12**, 158 (1929).

Determination of Glucose in Presence of Fructose and Glycine by Iodometric Method[1]

F. A. Dykins and D. T. Englis

Chemical Laboratory, University of Illinois, Urbana, Ill.

A study has been made of the effect of the presence of fructose and glycine upon the determination of glucose by oxidation with alkaline iodine solution in the presence of sodium hydroxide, sodium carbonate, and phosphate buffers.

The rate of oxidation is so rapid that the extent of condensation of the glucose and glycine is negligible under the conditions of the experiments, and there is no tendency for low results due to this cause if the solution is neutral when the analysis is begun.

The results obtained are always higher than those due to glucose alone because of reduction of iodine by the fructose and glycine.

Even if fructose may react immediately with the glycine, the compound has little protective action against the oxidizing agent.

Of the various basic reagents used with iodine, sodium phosphate has a number of advantages and gave the most satisfactory results.

The selective oxidation of aldol sugars by iodine in alkaline solution has received renewed attention on account of the ease and rapidity of the method (*10*) and its special application to the analysis for glucose in plant materials used as sources of fructose (*9*, *3*).

One of the objections assigned to the iodometric method is that it gives high results because of the fact that substances other than sugars take up iodine under the conditions of the analysis. On the other hand, certain factors may tend to cause low results. It has been demonstrated by Euler and Brunius (*5*, *6*), and Englis and Dykins (*4*) that when amino acids are present and the solution is alkaline, a stable condensation product of the monosaccharide sugars with the amino substances takes place and prevents its oxidation by iodine in alkaline solution. With glucose the rate of condensation is relatively slow near the neutral point but increases rapidly in rate and extent as the alkalinity is increased. With levulose the combination is immediate and at a lower alkalinity. If the amino substance can then combine with only an equal molecular quantity of sugar, it might be expected that since fructose is the predominating sugar in the hydrolyzed extracts of inulin-containing plants, it might combine with all the amino material and thus leave the aldol sugar to react as it normally would in the absence of the amino substance. If the amino substances still tend to react with the aldol sugar, the rate will be a function of the time, temperature, and alkalinity, and different values may be expected for the iodometric methods using different degrees of alkalinity and different reaction periods. To secure definite information upon these points was the object of these experiments.

[1] Received September 12, 1930.

Experimental Procedure

Three methods involving different basic reagents for the iodometric procedures were used. In the first, sodium hydroxide was the base and the conditions approximated those outlined by Kolthoff (*7*). In the second, sodium carbonate was utilized under about the same conditions as specified by Cajori (*1*) except that the quantities of reacting materials were increased about 2.5 times. In the third, a disodium phosphate–sodium hydroxide buffer mixture of about the same pH value as the sodium carbonate mixture was used.

The iodine and sodium thiosulfate solutions used were approximately 0.1 normal. The sodium thiosulfate solution was standardized against pure potassium dichromate and its value in terms of glucose was found to be 9.515 mg. per cc. In each series of determinations, blank runs were made in which distilled water replaced the sugar solution.

A concentrated stock solution of a high purity glucose containing 10.000 grams in 100 cc. was made the source of the glucose for all experiments. When 10 cc. of this were

Table I—Determination of Glucose in Presence of Fructose and Glycine by Iodometric Method

Alkali Used		Initial pH	Time Interval	Contents of 25 cc. Soln.	$Na_2S_2O_3$ Used		$Na_2S_2O_3$ Equiv. to I_2 Reduced	Apparent Glucose Found Attributed to:			
					Blank	Sugar soln.		Total	Glucose	Fructose	Glycine
	Cc.		*Minutes*	*Mg.*	*Cc.*	*Cc.*	*Cc.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
ALKALINE MEDIUM PRODUCED BY SODIUM HYDROXIDE											
0.5 *N* NaOH	8	12.40	10	Glucose 100	25.93	15.35	10.58	100.7	100.7	...	..
				Glycine 25	25.93	24.83	1.10	10.5	...	...	10.5
				Glucose 100, Fructose 200	25.93	14.50	11.43	108.8	100.7	8.1	..
				Glucose 100, Glycine 25	25.93	14.66	11.27	107.2	100.7	...	6.5
				Glucose 100, Fructose 200, Glycine 25	25.93	14.22	11.71	111.4	100.7	10.7	
ALKALINE MEDIUM PRODUCED BY SODIUM CARBONATE											
15% Na_2CO_3	5	11.43	25	Glucose 100	25.92	15.17	10.75	102.3	102.3	...	..
				Glycine 25	25.92	25.69	0.23	2.2	...	...	2.2
				Glucose 100, Fructose 200	25.92	14.30	11.62	110.6	102.3	8.3	..
				Glucose 100, Glycine 25	25.92	15.10	10.82	102.9	102.3	...	0.6
				Glucose 100, Fructose 200, Glycine 25	25.92	14.39	11.53	109.7	102.3	7.4	
ALKALINE MEDIUM PRODUCED BY SODIUM PHOSPHATE–SODIUM HYDROXIDE MIXTURE											
25% Na_2HPO_4 + $12H_2O$	10	11.48	60	Glucose 100	25.95	15.46	10.49	99.8	99.8	...	..
				Glycine 25	25.95	25.49	0.46	4.4	...	...	4.4
0.5 *N* NaOH	5			Glucose 100, Fructose 200	25.95	15.36	10.59	100.8	99.8	1.0	..
				Glucose 100, Glycine 25	25.95	15.20	10.75	102.3	99.8	...	2.5
				Glucose 100, Fructose 200, Glycine 25	25.95	15.22	10.73	102.1	99.8	2.3	

diluted to 250 cc., the solution was of a concentration such that 25 cc. then contained 100 mg. glucose. For the mixtures containing glycine and fructose, these reagents were added to the diluted glucose solution before it was made up to volume.

A sample of Pfanstiehl 90 per cent levulose was recrystallized from glacial acetic acid, washed with absolute alcohol, and dried in a vacuum oven. The crystals were perfectly white and the purity by polarization using Vosburgh's (*11*) formula was 99.7 per cent.

The purity of the glycine was first tested by observation of the melting point which was found to be 225–9° C. Reported values of 231–5° C. are given in the literature. However, due to the fact that decomposition takes place near the melting point, the test is not very satisfactory. To confirm further the purity of the sample used with the sugars in the experimental work which follows, comparative tests of its reactivity with iodine solution were made upon five different samples of glycine from both natural and synthetic sources. One of these had been analyzed for amino nitrogen by the Van Slyke method and the theoretical value found. All showed practically the same reducing power toward iodine as that of the sample indicated in the table. It seems safe to conclude that the reducing action is due to glycine and not to any impurity in the samples. The fact that alanine and aspartic acid show a similar reactivity adds evidence to this conclusion.

As pointed out by Kolthoff (*8*) it was found necessary to mix the sugar and iodine solutions before adding the alkali. Twenty-five cubic centimeters of each were measured into glass-stoppered flasks and to the mixture the alkali was added. The time of making the mixture alkaline was considered as zero time. The flasks were then stoppered and placed in the dark. After the reaction had proceeded the specified number of minutes, the solution was acidified with 0.5 *N* sulfuric acid and titrated at once with the standard thiosulfate solution. Details as to the amount and kind of alkali used, and the time allotted, as well as the results obtained, are tabulated in Table I.

Discussion

In Table I the same value for iodine reduced is assigned for the glucose of the sugar mixture as is obtained where glucose is present alone, and the difference from the total reduction obtained is attributed to the accompanying fructose or glycine or both. This figure is given for the purpose of indicating the error only, since the presence of the amino acid or fructose probably alters the reduction value of the glucose itself, and even greater values than those which are attributed to the accompanying substances in the table, are likely due to them.

As shown in the first section, the error due to the fructose and glycine is greatest when the alkalinity is highest and due to sodium hydroxide. In all cases the error is in the direction of high results rather than lower values as was anticipated. The glycine itself seems to have some reducing action which may be analogous to the Hoffman hypobromite reaction. The time interval for the reaction with the sugar is such that oxidation takes place before the condensation of glucose and glycine is appreciable. The fact that fructose combines immediately with amino substances may account for the decrease in the total reduction when both are present together with glucose, as is shown by the fact that the summation of the increments assigned to each is greater than the increment when both are present in the mixture.

Table II—Rate of Oxidation of Glucose in Alkaline Medium Produced by Sodium Phosphate–Sodium Hydroxide Mixture

Alkali used, 10 cc. 25% Na_2HPO_4 + $12H_2O$; initial pH, 11.48; 5 cc. 0.5 *N* NaOH

Time	$Na_2S_2O_3$ Used		$Na_2S_2O_3$ Equivalent to I_2 Reduced[a]	Glucose Present
	Glucose	Blank		
Minutes	*Cc.*	*Cc.*	*Cc.*	*Mg.*
0	25.98	25.98	0.00	0.0
10	16.32	25.97	9.65	91.8
20	16.05	25.97	9.92	94.4
30	15.65	25.95	10.30	98.0
40	15.60	25.95	10.35	98.5
50	15.52	25.94	10.42	99.1
60	15.45	25.95	10.50	99.9
75	15.39	25.95	10.56	100.5
90	15.30	25.93	10.63	101.1

[a] 1 cc. = 9.515 mg. glucose.

Although Colin and Lievin (*2*) in 1918 have used a phosphate buffer in connection with iodometric sugar determinations, they have made no critical study of it. Most of the recent work has been with sodium hydroxide or sodium carbonate. With the latter the brisk effervescence of carbon dioxide upon acidification increases the danger of loss of iodine by volatility. This fact, in addition to other favorable aspects, led to an experiment as to the effect of the time interval upon the extent of oxidation of the pure glucose with the phosphate buffer. The results are given in Table II.

Conclusion

It seems safe to conclude that the presence of amino substances will tend to give slightly higher values for glucose by the iodometric method and that the condensation reaction between the aldol sugar and amino acid will not have a significant effect unless the solution has been allowed to stand for some time in an alkaline condition before the analysis is made. Such a situation might follow a defecation procedure as has been pointed out in a previous paper.

On the whole the phosphate buffer gives more satisfactory results than a carbonate buffer of the same pH. The results vary but little over a considerable time interval; there is less danger of loss of iodine on acidification of the reaction mixture and less error due to the presence of fructose and amino substances.

Literature Cited

(1) Cajori, *J. Biol. Chem.*, **54**, 617 (1922).
(2) Colin and Lievin, *Bull. soc. chim.*, **23**, 403 (1918).
(3) Englis and Byer, Ind. Eng. Chem., Anal. Ed., **2**, 121 (1930).
(4) Englis and Dykins, *Ibid.*, **3**, 17 (1931).
(5) Euler and Brunius, *Z. physiol. Chem.*, **155**, 259 (1926).
(6) Euler and Brunius, *Ibid.*, **161**, 265 (1926).
(7) Kolthoff, *Z. Untersuch. Nahrungs Genussm.*, **45**, 131 (1923).
(8) Kolthoff, "Volumetric Analysis," Vol. 11, p. 446, Wiley, 1929.
(9) Oliver, University of Minnesota, M.S. Thesis, 1927.
(10) Slater and Acree, Ind. Eng. Chem., Anal. Ed., **2**, 274 (1930).
(11) Vosburgh, *J. Am. Chem. Soc.*, **42**, 1696 (1920).

Determination of Phosphates in Presence of Silica in Boiler Water[1]

Elwood W. Scarritt

Elgin Softener Corporation, Elgin, Ill.

THE greatest source of error in the colorimetric determination of phosphate in boiler waters and in other alkaline solutions is the interference of silica or silicate. Relatively minute quantities of silica cause the production of a blue color similar to the color due to phosphate. This interference has recently been noted by many workers in the boiler field. The present paper describes a method that minimizes this difficulty and produces reliable results in the presence of silica.

When the colorimetric method for phosphate determination was first used in this laboratory certain samples developed a clear blue color more like the blue of copper sulfate solution than the characteristic violet-blue of the phosphate when treated with slightly acidified molybdate and hydroquinone solutions, and subsequently neutralized with sodium carbonate in the presence of sodium sulfate. It had been suggested that iron interfered, but this was found not to be the cause of the clear blue color in the samples of boiler water, zeolite-softened well water, or certain untreated natural waters which contained no phosphate.

Investigation showed the color to be due to silica. The presence of silica also intensified the color due to phosphates in samples of known phosphate content, causing errors in the phosphate estimation as great as 100 per cent.

Since the blue color is proportional to the amount of phosphate or silicate ion in solution in the sample, it was obviously necessary to remove the silicate if the phosphate was to be determined accurately. It was not convenient to dehydrate or precipitate the silicate, but by acidifying to the right degree it was found possible to repress the ionization of the weak silicic acid to a point where it developed no noticeable blue color, while the stronger phosphoric acid remained sufficiently ionized to react with the molybdate and produce a blue color proportional in intensity to the concentration of phosphate present.

It is important to make up the phosphate standards with the same amount of acid used in testing the samples, as the quantity of acid used influences the depth of color produced.

Solutions Required

(1) Standard sodium phosphate, $Na_3PO_4.12H_2O$—0.320 gram per liter. 1 ml. = 2 p.p.m. PO_4 in 40 ml. H_2O.

(2) Sulfuric acid—600 ml. H_2O plus 300 ml. 95% c.p. H_2SO_4.

(3) Ammonium molybdate, $(NH_4)_6 Mo_7O_{21}.4H_2O$—92.3 grams per liter plus 38 ml. concd. H_2SO_4.

(4) Hydroquinone, $C_6H_6(OH)_2$—23 grams per liter plus 5 ml. concd. H_2SO_4.

(5) Alkaline sodium sulfite—183 grams NaOH + 16 grams Na_2SO_3 per liter H_2O.

Procedure

To a 40-ml. sample to be tested for phosphate, add 5 ml. sulfuric acid and mix thoroughly. Add 1 ml. of molybdate solution and 1 ml. of hydroquinone solution. Again shake vigorously and allow to stand 5 minutes. Then add 15 ml. of the alkaline sodium sulfite. If phosphate is present a blue color will form which is then compared with standards of known PO_4 content prepared in exactly the same way as the sample being analyzed.

For general laboratory analysis it is found convenient to make up standards of 5, 10, 20, 30, 40, and 50 p.p.m. In the boiler room, however, it is usually sufficient to prepare only two standards representing the upper and lower limits of allowable PO_4 concentration. If the color developed in the boiler water is less than 20, for example, more sodium phosphate should be fed. If the color is greater than 30, the addition of phosphate may be curtailed.

Large test tubes of uniform size or 100-ml. Nessler tubes will be found convenient for comparing the colors. The comparison should be made at once since the phosphate color begins to fade after about 10 minutes. There is also a tendency for the silicate color to appear if the sample is allowed to stand 5 to 10 minutes after neutralizing the acid with the alkaline sulfite solution.

[1] Received September 4, 1930.

Determination of Copper in Dairy Products[1,2]

H. T. Gebhardt and H. H. Sommer

Department of Dairy Husbandry, University of Wisconsin, Madison, Wis.

A new method for the determination of copper in foodstuffs and biological material has been devised. It was found that the method of Elvehjem and Lindow could be shortened considerably, the separation of copper sulfide improved, and the danger of losses in transfers minimized, by shaking out the precipitated copper sulfide with chloroform instead of separating it by filtering. It was found that the ashing temperature and time used may be the source of large errors in copper determinations. The ashing temperature should not exceed 565° C. for 3 to 4 hours.

Detailed directions for the procedure, embodying precautions as to ashing conditions, and the modification mentioned, are given. The detailed method as outlined gives results that agree closely with those obtained by the original Elvehjem-Lindow method, when the latter is used with the necessary precautions as to ashing conditions.

IN THE past, copper has been considered toxic or undesirable in foods, but today it is generally known that copper is an essential constituent of most plant and animal material, and that it plays an important role in life processes. This has been definitely shown by the recent work by Hart and co-workers (*5*) on the function of minute amounts of copper in foods in the cure of nutritional anemia. This recent work has opened an important field for further studies of the functions of this element in life processes, and its distribution in living material.

However, in the manufacture of many foodstuffs, it is still desirable to keep the copper content at a minimum for technical, if not legal, reasons. This is especially true in the case of dairy products, where the detrimental effect of copper has long been known, but not fully appreciated until the recent work of Guthrie (*4*). A method for determining the copper content of foodstuffs is therefore of general and current interest.

The method given in this paper was developed in connection with experimental work to determine the solubility of copper in milk. However, the details evolved are applicable to the analysis of other foodstuffs and biological materials. The method as given is a modification of the Elvehjem-Lindow (*3*) method for the determination of copper in biological materials, which in turn was based on the method of Biazzo (*2*) for the copper determination in canned vegetables.

Methods Previously Used

Recent work on the distribution of copper in foodstuffs and biological materials has become possible only through the development of the colorimetric methods which permit the estimation of minute amounts of copper in relatively small samples. Previous to this, electrolytic methods had been used most frequently, but for samples containing mere traces of copper these methods were unsatisfactory because of the large samples required to obtain a weighable deposit, and because of the other ash constituents which frequently interfered with the copper deposition.

The colorimetric methods which have been developed to overcome these difficulties have been used in analyses to determine the copper content of raw milk and the amount of copper dissolved by milk from dairy equipment. The potassium ethylxanthate method was adapted to the determination of copper in milk by Supplee and Bellis (*9*) and this adaptation was used by King and Etzel (*6*), Quam and coworkers (*7*), and, in combination with the electrolytic method, by Rice and Miscall (*8*). The colorimetric method developed by Elvehjem and Lindow for the determination of copper in biological materials is more recent. It is based on the color reaction given by copper with potassium thiocyanate and pyridine, which is very specific, and the color in the chloroform solution is proportional to the amount of copper present.

Observations Leading to Modified Method

The method of Elvehjem and Lindow was tentatively selected mainly because the reagents were available.

The accuracy of the method was tested by making a large number of recovery determinations; but the results were disappointing. Not more than 55 to 70 per cent of the added copper was recovered, even when the directions of the method were followed in detail.

To find the cause of the losses of copper during the procedure, efforts were made to induce more complete and rapid flocculation of the copper sulfide, but no improvements in the percentage of recovery were attained. Removing the iron and phosphate in the manner of Supplee and Bellis (addition of an excess of ammonium hydroxide to the ash solution and filtering) and making the colorimetric determination directly on the concentrated filtrate did not give the desired recovery, thus indicating that copper was lost at some other step in the procedure.

When the copper was added to the milk ash solution, recovery was greatly improved. This finding, together with the observation that any attempt to obtain a whiter ash by using higher ashing temperatures and longer times was followed by lower results, called for improvement of the ashing procedure.

In further determinations the ashing temperature was confined to a range of between 510° and 565° C. Using this temperature, ashing was completed in about 3 to 4 hours. Under these conditions results given in Table I were obtained.

Table I—Copper Determinations in Skim Milk with and without Added Copper Using Ashing Temperature of 510° to 565° C.

Sample	Skim Milk Used	Copper Added	Colorimeter Readings		Copper Indicated	Added Copper Recovered
			Standard[a]	Unknown		
	Cc.	*Mg.*	*Mm.*	*Mm.*	*Mg.*	%
1	250	0.0	5.00	12.27	0.041	91.0
	250	0.0	5.00	12.88	0.039	
	250	0.1[b]	13.00	9.98	0.130	
	250	0.1[b]	13.00	9.87	0.132	
2	250	0.0	2.90	10.50	0.028 (0.0235)[d]	96.65[d]
	250	0.0	3.45	11.53	0.030 (0.0252)[d]	
	210	0.1[c]	10.00	8.27	0.121	

[a] Color standard 0.1 mg. copper in 5 cc. chloroform.
[b] Copper added to ash solution.
[c] Copper added to skim milk before ashing.
[d] Figured to basis of 210-cc. milk sample.

The addition of 0.1 mg. copper to the ash solution of sample 1 increased the result of the analysis from 0.040 to 0.131 mg., or an increase of 0.091 mg. This represents a recovery of the added copper of 91 per cent. In sample 2

[1] Received March 28, 1930; revised paper received September 24, 1930.
[2] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

the addition of 0.1 mg. copper to the skim milk before ashing increased the result of the analysis from 0.02435 to 0.1210 mg. copper, or an increase of 0.09665 mg. This represents a recovery of added copper of 96.65 per cent. These results indicate that the ashing procedure used had not caused the loss of any copper. The possibility of losing copper in ashing and the suitability of a low ashing temperature is further illustrated in Table II.

Table II—Effect of Ashing Conditions on Copper Determinations

Whole Milk[a] Used	Copper Added	Ashing Temp.	Ashing Time	Colorimeter Readings		Copper Indicated	Added Copper Recovered
				Standard[b]	Unknown		
Cc.	*Mg.*	*° C.*	*Hrs.*	*Mm.*	*Mm.*	*Mg.*	*%*
250	0.0	700–840	3	1.00	7.22	0.014	
250	0.1	700–840	3	5.00	11.22	0.045	31.0
250	0.0	510	8	3.00	8.89	0.034	
250	0.1	510	8	5.00	4.43	0.113	79.0

[a] The same milk was used throughout.
[b] The color standard contained 0.1 mg. copper in 5 cc. chloroform.

From the results in this table it is clear that a large fraction of the copper may be lost in ashing due to high ashing temperature or excessive time. The low percentage recovery of added copper, even where an ashing temperature of 510° C. was used, is due to the prolonged ashing, the results differing from those of Table I where the ashing time was 3 to 4 hours. It is probable that part of this loss is caused by the copper fusing with the silica dishes that were used, and part to volatilization.

With the importance of the ashing temperature and time recognized and carefully controlled, it was now decided to compare the original method of Elvehjem and Lindow with the modified form of this method, the modification consisting, as already stated, in the removal of the interfering iron and phosphate in the manner of Supplee and Bellis. The comparison of the results obtained by the two methods showed good agreement in a reasonably large number of experiments. On the average the original Elvehjem-Lindow method gave slightly higher results.

In the study to which this work on methods was incidental, both methods have been used, and both served quite well for the routine determinations, provided the precautions as to ashing temperature and time were observed. However, both methods require considerable time. The desire to shorten the time finally led to the use of chloroform to shake out the copper sulfide precipitated from the ash solution instead of allowing it to stand to flocculate, and then filtering.

Chloroform has been used for removing the colloidal copper sulfide to facilitate the reading of the end point in the volumetric titration of copper with ammonium sulfide (*1*). It was found that this procedure could be applied advantageously instead of filtering for the removal of the copper sulfide precipitate from the milk ash solution. A considerable saving of time is effected and, as will be shown, there is no sacrifice in accuracy.

Method for Determination of Copper in Milk

A 250-cc. portion of the sample is carefully evaporated over a low flame in a quartz evaporating dish. The addition of 10 to 15 drops of glacial acetic acid prevents film formation and foaming, and thus hastens evaporation. After evaporation of most of the moisture, the drying is completed in an oven at 150° to 200° C. When the sample has been thoroughly dried, as indicated by the caramelized or even charred appearance, it is transferred to an electric ashing furnace, the temperature of which should not exceed 565° C. The use of a pyrometer so that the ashing may be conducted at a known temperature is advisable. At this temperature ashing is usually complete in 3 to 4 hours, and a grayish white ash is obtained.

The ash is moistened with 4 cc. of dilute hydrochloric acid (1 to 1), and diluted to about 100 cc. with distilled water. To bring about complete solution, the solution in the quartz evaporating dish is heated and kept near the boiling point for about 20 minutes. It is then filtered, the dish and filter carefully washed with distilled water, and the filtrate and washings collected. The undestroyed carbon together with the filter paper is returned to the quartz dish and ashed for 30 minutes; the ash is dissolved in a few drops of dilute hydrochloric acid, diluted with distilled water, and warmed, filtered, and washed as before, the filtrate and washings being added to the main ash solution.

The total ash solution, or an aliquot thereof, if the copper content is expected to be high, is evaporated to about 10 cc. and transferred to a 25-cc. volumetric flask. Complete transfer is aided by adding a drop of dilute hydrochloric acid (1 to 1) to the first rinsing, and by heating this solution to boiling. After cooling to about room temperature, hydrogen sulfide is passed into the solution in the volumetric flask for 5 minutes through a capillary glass tube (a 4- or 5-mm. glass tube drawn out to a capillary of about 1 mm. outside diameter). The capillary should not be immersed in the solution until the hydrogen sulfide has been turned on, to prevent the solution from rising in the capillary; for the same reason it is advisable to remove the capillary from the solution before shutting off the hydrogen sulfide. The outside of the capillary is rinsed with 0.5 cc. of saturated hydrogen sulfide water. The flask is stoppered and set in cold water or otherwise cooled to about 10° C. To this cooled solution containing the precipitated copper sulfide, 5 cc. of chloroform, which has previously been cooled to about 10° C., are added, the flask is securely stoppered and shaken vigorously for about 1 minute. The flask is then set in cold water and the chloroform allowed to settle out. The water layer becomes perfectly clear, and the copper sulfide is now contained in the chloroform at the bottom of the flask.

The water solution is drawn off by means of a capillary tube, leaving enough to avoid the possibility of drawing out some of the chloroform. The remainder is diluted with 15 to 20 cc. of cold, saturated hydrogen sulfide water, and this is again drawn out as completely as possible. This one washing has been found sufficient in all cases; it can be omitted entirely if the aliquot does not represent more than the ash of 50 cc. of milk. The small amount of phosphate which is left in the solution in this case dissolves completely in the acetic acid added later in the colorimetric determination. Gas bubbles may make the removing of the water portion difficult if the temperature during the operations is too high.

It is desirable to limit the volume of the ash solution to 10 cc. as directed above, so that after the addition of the chloroform there is ample space for thorough shaking. The capillary tube which is used to draw out the water solution should not touch the side of the neck, because a fine film of chloroform containing copper sulfide usually covers the glass.

After the copper sulfide is shaken out with chloroform, the water solution drawn off, and the residue rinsed as directed, the chloroform is evaporated by placing the flask in a hot water bath for 10 minutes, increasing the temperature to boiling towards the end. The residue in the flask is dissolved by adding 1 cc. of concentrated nitric acid, placing the flask in the hot water bath for 20 minutes with occasional shaking to bring the acid in contact with the entire inside surface of the flask. The solution is then neutralized with dilute sodium hydroxide (200 grams in 1 liter of solution) so that the reaction is just alkaline phenolphthalein. The neck of the flask must be rinsed carefully to remove every trace of nitric acid (also oxides of nitrogen) which would interfere with the color reaction later. The indicator should

not be added too soon, because the compound formed by the destruction of phenolphthalein by strong acid or alkali dissolves in chloroform with a yellow color, and thus interferes with the colorimetric determination even if present only in traces. In the above neutralization, the indicator may be added after the first permanent turbidity develops due to the precipitation of traces of phosphate remaining in the flask. When this point has been reached, one drop of dilute sodium hydroxide solution then usually suffices to make the solution just alkaline to phenolphthalein.

From this point in the procedure the colorimetric determination as given by Elvehjem and Lindow is followed. To the neutralized solution in the flask, containing the dissolved copper sulfide, 1 cc. of glacial acetic acid, 1 cc. of a 10 per cent solution of potassium thiocyanate, and 10 drops of pyridine are added in the order given, with slight shaking after each addition. Finally 5 cc. of chloroform, accurately measured, are added, and the volume made up to the mark with distilled water. After thorough shaking, the chloroform has taken up the green copper-thiocyanate-pyridine compound. The water portion is then removed by drawing off with a capillary tube, and the chloroform solution is used for the colorimetric comparison with a standard in a suitable colorimeter.

Table III—Results Obtained by New Method and Elvehjem-Lindow Method Using Ashing Temperatures of 510° to 565° C. and Ashing Times of 3 to 4 Hours

Sample	Elvehjem-Lindow Method (A)			New Method (B)			Deviation of B from A	
	Aliquot taken of ash soln. of 250 cc. milk	Copper detd. in aliquot	Copper	Aliquot taken of ash soln. of 250 cc. milk	Copper detd. in aliquot	Copper	Copper detd. in aliquot	Copper
		Mg.	*Mg./l.*		*Mg.*	*Mg./l.*	*Mg.*	*Mg./l.*
1	0.25	0.054	0.864	1/4	0.054	0.864	0.000	0.000
2	0.25	0.251	4.016	1/4	0.251	4.016	0.000	0.000
3	0.25	0.226[b]	3.616	1/4	0.263	4.208	+0.0370	0.592
4	0.40	0.050	0.500	2/5	0.053	0.530	+0.0030	0.030
5[a]	0.20	0.048	0.480	2/5	0.049	0.490	+0.0025	0.025
				2/5	0.052	0.520		
6[a]	0.25	0.054	0.432	1/4	0.055	0.440	+0.0015	0.012
				1/4	0.056	0.448		
7[a]	0.25	0.104	0.832	1/4	0.103	0.824	+0.0005	0.004
				1/4	0.105	0.848		
8[a]	0.25	0.065	0.520	1/4	0.067	0.536	+0.0075	0.060
				1/4	0.078	0.624		
9	0.25	0.041	0.656	1/4	0.043	0.688	+0.0025	0.040
				1/4	0.044	0.704		
10	0.25	0.019	0.304	1/4	0.020	0.320	+0.0015	0.024
					0.021	0.336		
11	0.25	0.096	1.536	1/4	0.103	1.648	+0.0110	0.168
				1/4	0.110	1.760		
12	0.40	0.070	0.700	2/5	0.072	0.720	+0.0020	0.020
				1/5	0.036	0.720		
13	0.25	0.094	1.504	1/4	0.104	1.664	+0.0100	0.160
14	0.25	0.073	1.168	1/4	0.066	1.056	−0.0070	0.120
15	0.016	0.051	12.750	2/125	0.047	11.750	−0.0040	1.000
16	0.02	0.047	9.400	1/50	0.050	10.000	+0.0030	0.600

[a] 500 cc. milk had been used for ashing.
[b] Sample was turbid and colorimetric readings less exact. This accounts for wide discrepancy in results. With amounts of copper as in samples 2 and 3, turbidity is likely to develop in 5-cc. chloroform solution. Exact point at which this occurs varies with temperature and salts present.

The standard for comparison is made from a stock solution made by dissolving 0.3928 gram of pure crystalline copper sulfate, $CuSO_4.5H_2O$, in distilled water and diluting to 1 liter. This stock solution contains 0.1 mg. of copper in each cubic centimeter. In making up the standard for comparison, enough of this stock solution should be used so that the standard contains approximately the same amount of copper as the unknown. If the copper content of the unknown is from 0.05 to 0.15 mg., take 1 cc. of the stock solution, add 1 cc. of glacial acetic acid, 1 cc. of 10 per cent potassium thiocyanate solution, and 10 drops of pyridine, and proceed as already described for the unknown sample. The standard for comparison will finally consist of 5 cc. chloroform with an amount of copper-thiocyanate-pyridine compound dissolved in accordance with the amount of stock solution used.

In working at low room temperatures, the colorimetric comparisons are frequently seriously influenced by the tendency of the standard to become turbid. Slight warming will cause the standard to become clear, but on cooling it again becomes cloudy. This difficulty may be overcome entirely by adding 1 cc. of concentrated nitric acid in making up the standard; the solution is then neutralized to phenolphthalein with dilute sodium hydroxide before adding the glacial acetic acid, potassium thiocyanate and pyridine, and shaking out with chloroform.

Comparison of New Method with Elvehjem-Lindow Method

Before the method, as outlined above, was finally adopted for the routine analyses in the problem under investigation, the copper content of a number of samples of milk, contaminated by varying amounts of copper, was determined by both methods. These results are given in Table III.

When the results given in this table are compared, it it must be considered that minute amounts of copper are being dealt with and that the final determinations are by colorimetric comparisons. In view of this, it may be concluded, first, that the results obtained by the two methods agree closely, and, second, that the results obtained by method B are slightly higher in the majority of cases and in the average. This slightly higher result by method B must be expected because there is obviously less opportunity for losses by transfers in method B, and because it was observed that the chloroform removed additional copper sulfide from the filtrate of the copper sulfide precipitation as used in method A.

From the above, and from results of recovery determinations made with the new method, and as shown in Table IV, it is apparent that the modifications introduced in the new method do not impair the accuracy of the original method. The advantages of the new method appear to be the saving of considerable time, reduced danger of contamination and of losses in transfers, and more complete separation of the copper sulfide.

Table IV—Copper Determinations in Milk with and without Added Copper Using Ashing Temperatures of 510° to 565° C.

Sample	Milk Ashed	Copper Ashed to Milk	Colorimeter Readings: Standard: Copper	Colorimeter Readings: Standard: Reading	Colorimeter Readings: Unknown reading	Copper Indicated	Added Copper Recovered
	Cc.	*Mg.*	*Mg.*	*Mm.*	*Mm.*	*Mg.*	%
1	250	0.00	0.05	10.0	12.22	0.0409	
	250	0.10	0.10	10.0	7.34	0.1363	95.4
	250	0.10	0.10	10.0	6.47	0.1545	113.6
2	250	0.00	0.10	2.0	14.00	0.0143	
	250	0.15	0.10	10.0	6.73	0.1487	89.6
	250	0.20	0.10	10.0	4.85	0.2062	96.0
3	250	0.00	0.03	10.0	11.39	0.0264	
	250	0.10	0.10	10.0	8.50	0.1177	91.3
	250	0.10	0.10	10.0	8.37	0.1195	93.1
	250	0.05	0.10	8.0	10.56	0.0758	98.8

Literature Cited

(1) Beckhurts, H., "Die Methoden der Massanalyse," p. 875, Vieweg, Braunschweig, 1913.
(2) Biazzo, R., *Ann. chim. applicata*, **16**, 2 (1926).
(3) Elvehjem, C. A., and Lindow, C. W., *J. Biol. Chem.*, **81**, 435 (1929).
(4) Guthrie, E. S., unpublished paper.
(5) Hart, E. B., Steenbock, H., Wadell, J., and Elvehjem, C. A., *J. Biol. Chem.*, **77**, 797 (1928).
(6) King, C. G., and Etzel, G., Ind. Eng. Chem., **19**, 1004 (1927).
(7) Quam, G. N., Soloman, E. I., and Hellwig, A., *Ibid.*, **20**, 930 (1928).
(8) Rice, F. E., and Miscall, J., *J. Dairy Sci.*, **6**, 261 (1923).
(9) Supplee, G. C., and Bellis, J., *Ibid.*, **5**, 455 (1922).

Electrolytic Determination of Lead as Lead Dioxide[1]

W. T. Schrenk and Philip H. Delano

Missouri School of Mines and Metallurgy, Rolla, Mo.

The electrolytic method for the determination of lead has been studied and the best results were obtained when the following conditions were observed: The sample should be electrolyzed for $1^1/_2$ to 2 hours with a current of 3 amperes and placed on the board at a temperature of 90° C. The anodes should be sand blasted and clean and the amount of lead present between 5 and 150 mg. The solution should contain from 20 to 30 per cent free nitric acid and about $^1/_4$ cc. of sulfuric acid. Interfering elements should be absent.

The effects of interfering impurities were investigated and silver, bismuth, manganese, tin, arsenic, antimony, mercury, chromate, and phosphate were found to cause poor results. If these elements are present in any great amount, a separation should be made before electrolyzing. Potassium, sodium, ammonia, calcium, magnesium, cadmium, copper, zinc, and iron were found to have no effect unless the solution contains large amounts of the salt.

The precision of the method was determined. It was found that the average variation obtained was less than 0.2 mg. provided the lead content of the sample is between 5 and 150 mg. Samples of higher lead content can be run but the error is usually somewhat larger. The error is practically always negative. The theoretical factor should always be used with this method in order to avoid low results.

THE electrolytic method for lead has been adopted as a control method especially for ores in which the lead content is less than 7 per cent. The method is rapid and accurate under certain conditions but variations in conditions produce erratic and irregular results which may check each other but will not check the true lead content.

Because of this fact a thorough study of the conditions affecting the electrolytic deposition of lead dioxide was undertaken. The following factors may affect the determination of lead: (1) apparatus, (2) temperature, (3) time of electrolysis, (4) concentration of acid, (5) current, (6) amount of lead present, (7) added reagents, and (8) type of material analyzed.

Apparatus and Solutions

A slight modification of the apparatus first used by Guess (*1*), and further described by Holmes and Morgan (*2*), was used in this work. A diagram of the apparatus is given in Figure 1.

The anodes should be made of 0.005-inch (0.0127-cm.) sand blasted sheet platinum. Sleeves of rubber tubing placed over the split terminals furnish contact pressure to hold the anodes and cathodes in place. The cathodes are firmly held in place by an additional bakelite sleeve placed over the end of the terminal. The cathodes are stiffer and last longer if crimped as shown. The terminals should be of rolled hard drawn aluminum in order to resist the acid fumes to which they are exposed. The base may be either cast or machined but the terminals should be welded to it to insure against poor contact. The wiring should be so arranged that any number of cells may be removed from the board without disturbing the remaining cells. The wiring in the diagram has this advantage.

Lead nitrate was prepared by dissolving pure lead in nitric acid. The solution was filtered through a quartz filter, and precipitated with concentrated nitric acid. The recrystallization was repeated several times and the salt dried. Solutions of known lead content were prepared from this purified lead nitrate and checked gravimetrically by the sulfate method.

[1] Received September 5, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Preliminary Procedure

In the preliminary experiments the conditions were selected which had been recommended by other workers and had been used in this laboratory. All factors were held constant save one which was varied and the effect of this variable was studied. The procedure at first used was to take a suitable weight of the sample and digest with 20 cc. of nitric acid. When brown fumes ceased to be evolved, 15 cc. of a saturated solution of ammonium nitrate was added and the solution boiled for approximately 1 minute. The sample was then diluted with cold water and electrolyzed for $1^1/_2$ to 2 hours. If a pure lead solution were used instead of a

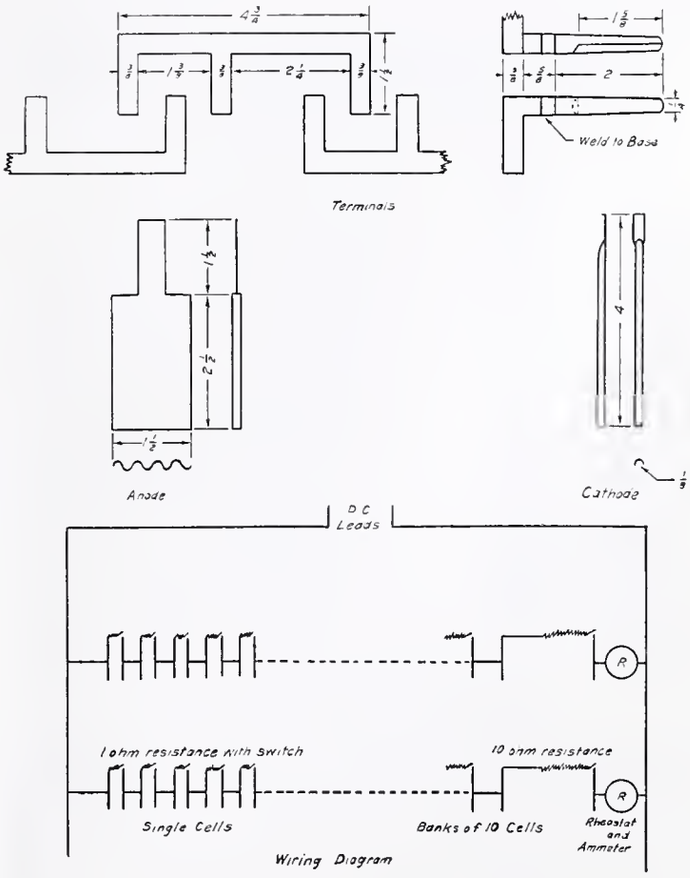


Figure 1

standard sample, the procedure was approximately the same.

Effect of Time and Temperature

The usual value for current with the type of anodes used in these experiments is 3 amperes (a current density of about 7 amperes per square decimeter), giving good results in $1^1/_2$ to 2 hours. It was found that complete deposition in the cold could only be secured by electrolysis over a period of 8 or more hours, the slowness of deposition being due to the plating of lead on the cathode. Electrolysis of a solution at an initial temperature of 90° to 95° C. yielded a quantitative deposition of lead in a period of $1^1/_2$ to 2 hours. The temperature during this time dropped to about 50° C. The lead is not completely deposited from the solution if the high temperature is maintained during the electrolysis.

Table I—Effect of Time and Temperature

Conditions of experiment: 140 cc. soln.; 30 cc. HNO_3; 3 amperes

	Gram
PbO_2 taken	0.0288
Average of 8 determinations (cold) $1^1/_2$ hours	0.0254
Maximum deviation from average	0.0003
Error	0.0034
PbO_2 taken	0.0250
Average of 6 determinations (cold) 8 hours	0.0249
Maximum deviation from average	0.0002
Error	0.0001
PbO_2 taken	0.0250
Average of 22 determinations (hot) $1^1/_2$ hours	0.02501
Maximum deviation from average	0.0002
Error	0.00001

These results, given in Table I, indicate that the temperature is one of the most important factors in the electrolysis of a lead solution. Results in the cold are poor unless a long period of electrolysis is used, while results with a hot solution are very good in $1^1/_2$ to 2 hours. The experiments also brought out the fact that checking results could be obtained under practically all conditions, even though all of the lead was not deposited from the solution. This emphasizes the fact that checking results do not mean quantitative results.

Table II—Effect of Ammonium Nitrate, Nitric Acid, and Sulfuric Acid

Conditions of experiment: 140 cc. soln.; 90° C.; 2 hours; 3 amperes

PbO_2 Taken	PbO_2 Found	NH_4NO_3	HNO_3	H_2SO_4	Remarks
Gram	*Gram*	*Cc.*	*Cc.*	*Cc.*	
0.0025	0.0009	..	10	....	
0.0025	0.0016	..	20	....	
0.0025	0.0014	..	30	....	
0.0250	0.0096	..	10	....	
0.0250	0.0238	..	20	....	
0.0250	0.0250	..	30	....	
0.1156	0.1125	..	15	....	
0.1156	0.1148	..	30	....	
0.0188	0.0182	..	30	....	
0.0469	0.0454	..	30	....	
0.1407	0.1351	..	30	....	
0.0188	0.0175	15	30	....	
0.0469	0.0452	15	30	....	
0.1407	0.1384	15	30	....	
0.0188	0.0187	..	30	8 drops	
0.0469	0.0470	..	30	8 drops	
0.1407	0.1410	15	30	8 drops	
0.2887	0.2864	..	30	....	Slight scaling
0.2887	0.2806	15	30	....	Scaling increased
0.2887	0.2876	..	30	8 drops	
0.2887	0.2878	15	30	8 drops	
0.1156	0.1155	..	30	0.5 cc.	
0.1156	0.1156	..	30	1.5 cc.	
0.1156	0.1154	15	30	1.5 cc.	
0.1156	0.1155	15	30	2.5 cc.	
0.1156	0.1156	..	30	2.5 cc.	
0.1156	0.1080	15	30	5 cc.	Very low results
0.1156	....	15	30	30 cc.	No deposit

Effect of Acid Concentrations

The series of experiments to determine the effect of acid concentrations brought out the fact that complete deposition is best secured when from 20 to 30 per cent free nitric acid is present. A series of experiments was run to determine the effect of sulfuric acid and the sulfate ion. From 0.25 to 0.5 cc. of sulfuric acid aided the deposition materially by giving a firmer and more coherent deposit and increasing the amount of lead dioxide which could be quantitatively determined. A concentration of sulfuric acid in greater amounts than 2.5 cc. produces incomplete deposition. The concentration of sulfate ion produced by the addition of sodium sulfate, potassium sulfate, or calcium sulfate produced the same effect as did sulfuric acid. When running a sulfide ore there is always a little sulfate present, either from the original ore or formed by the action of the nitric acid during the solution of the sample. This sulfate probably explains the excellent results usually obtained in the electrolytic analysis of sulfide ores.

In these experiments, noted in Table II, it was demonstrated that ammonium nitrate is not essential and in larger amounts tends to produce scaling. Also it has been found that satisfactory results are obtained when the electrodes are dried rapidly on a hot plate or in an oven at a temperature between 150° and 200° C. The anodes are removed from the hot plate as soon as dry.

Interfering Elements

The effect of certain salts on the deposition of lead dioxide was studied. The salts were those which might be obtained in the solution of a lead ore. Calcium nitrate, cadmium nitrate, zinc nitrate, potassium nitrate, sodium nitrate, cupric nitrate, ferric nitrate, and perchloric acid were without effect when sulfuric acid was present.

Certain elements, however, do interfere with the determination. An investigation of the effects of silver, bismuth, arsenic, antimony, mercury, manganese, tin, chromate, and phosphate shows them to be harmful to the determination. Some of these impurities deposit with the lead while others prevent deposition or cause scaling of the lead dioxide deposit. In any case in which these elements are present in an amount large enough to cause trouble, a separation must be performed. Traces of these impurities may be present without the production of any appreciable interference. The results of this investigation are given in Table III.

A small amount of chromate does not harm the determination so that it would be possible to precipitate lead from solution as lead chromate, redissolve, and deposit electrolytically as lead dioxide.

Table III—Effect of Interfering Elements

Conditions of experiment: 30 cc. HNO_3; 1.5–2 hours; 3 amperes; 0.25 cc. H_2SO_4; 90° C.; 140 cc. soln.

Impurity Present	Weight of Impurity	PbO_2 Taken	PbO_2 Found	Remarks
	Gram	*Gram*	*Gram*	
As	0.0050	0.0100	0.0064	
	0.0100	0.0500	0.0416	
Mn	0.0300	0.0100	0.0108	Deposit with PbO_2 loosens deposit
	0.0200	0.0500	0.0504	
	Scaling with large amounts of Mn			
Bi	0.0050	0.0500	0.0524	Deposit with PbO_2 may loosen deposit
	0.0100	0.0500	0.0550	
	0.0500	0.0500	Scaling	
Sn	0.2500	0.0500	0.0552	
	0.5000	0.0500	0.0590	
Sb	0.0100	0.0500	0.0520	
	0.1000	0.0500	0.0494	
Ag	0.0100	0.0500	0.0506	Deposits with PbO_2
	0.1000	0.0500	0.0510	
Hg	0.0100	0.0500	0.0426	Hg on cathode holds Pb
	0.1000	0.0500	0.0422	
CrO_4	0.0500	0.1156	0.1157	Occluded
	0.2500	0.1156	0.1168	
	1.0000	0.1156	0.1186	
H_3PO_4	1 cc.	0.0500	Very low	
	5 cc.	0.0500	No deposit	
Na_2HPO_4	0.0500	0.1156	0.1147	
	0.2500	0.1156	0.1100	
	0.5000	0.1156	0.0980	

Amount of Lead

The amount of lead which may be quantitatively deposited was determined and the data presented in Table IV and Figures 2 and 3. These indicate that the method gives

excellent results when the lead content of the sample is between 5 and 150 mg. Within this range the average error of the method is less than 0.2 mg. of lead. When the sample contains less than 5 mg. of lead, low results are obtained. Should the lead content of the solution be more than 150 mg., as much as 1 mg. of lead may remain in solution.

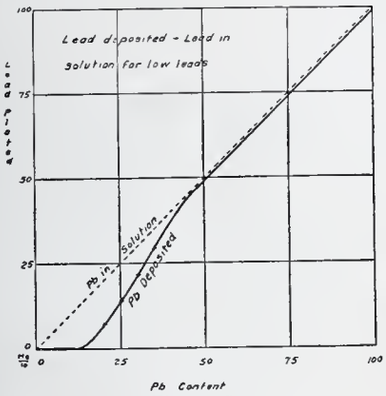


Figure 2

Other workers have recommended factors less than theoretical. According to this the method should give high results when the theoretical factor is used, but in these experiments high results were never obtained unless some interfering element, such as bismuth or tin, were present. The factor lead taken over lead dioxide deposited, is always 0.8662 if the proper conditions are observed. Hydrogen sulfide was used to test for the complete deposition of lead and only traces were found after electrolysis.

Table IV—Deposition of Various Amounts of PbO_2

Conditions of experiment: 140 cc. soln.; 0.25 cc. H_2SO_4; 2 hours; 3 amperes; 90° C.; 35 cc. HNO_3

PbO_2 Taken	PbO_2 Found	No. of Detns.	Average Deviation
Gram	*Gram*		*Gram*
0.0015	0.0000	2	.....
0.0020	0.0010	3	.....
0.0025	0.0012	5	0.0013
0.0030	0.0022	1	0.0008
0.0035	0.0028	1	0.0007
0.0040	0.0036	5	0.0004
0.0045	0.0044	1	0.0001
0.0050	0.0049	4	0.0001
0.0075	0.0076	2	0.0001
0.0100	0.0100	2	0.0000
0.0250	0.02501	22	0.00001
0.1156	0.11555	18	0.00005
0.1732	0.1727	5	0.0005
0.2309	0.2295	3	0.0014
0.2887	0.2876	5	0.0012
0.3464	0.3451	4	0.0013
0.4041	0.4024	5	0.0017

Procedure

The procedure as finally adopted and recommended for use when there is no interference from other elements is as follows: A sample, the amount depending upon the per cent of lead, is weighed into an ordinary 150 cc. electrolytic beaker, 30 to 35 cc. of nitric acid are added, and the sample is boiled until brown fumes cease to be evolved. The sides of the beaker are washed and 0.25 cc. sulfuric acid added. The solution is boiled again for 1 to 2 minutes, diluted to 140 cc., and heated to a temperature of 90° C. It is then electrolyzed for 2 hours at 3 amperes. The anodes are removed from the board, washed in water, alcohol, dried rapidly in an oven or on a hot plate, cooled, and weighed. The weight of lead dioxide deposited is equal to the per cent of lead when a factor weight of the sample has been used. When interfering elements are present, it is necessary to perform a separation before electrolyzing.

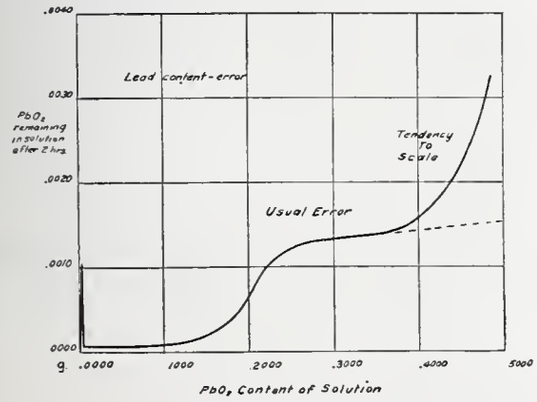


Figure 3

In applying this method to the analysis of lead concentrates it is usually best to take a one-fourth factor weight sample. A one-half factor weight sample may be run but the error is usually greater. Care must be taken to assure a homogeneous sample. In some instances it is necessary to grind the sample to pass a 200-mesh screen before satisfactory results can be obtained.

This is illustrated by the data given in Table V.

Table V—Analysis of Lead Concentrates

Original Sample 100-Mesh	Sample 150-Mesh	Sample 200-Mesh
%	%	%
51.76	53.88	53.92
53.76	53.68	53.92
53.96	53.60	54.04
53.92	53.76	53.88[a]
54.46	53.88	53.84[a]
53.72	54.08	53.84[a]
53.44		Av. 53.91 ± 0.05
53.48		
54.46		
53.42		
53.90		
53.90		

[a] Run by A. W. Holmes, Bureau of Mines.

Literature Cited

(1) Guess, *Bull. Am. Inst. Mining Eng.*, 1239 (1905).
(2) Holmes and Morgan, Ind. Eng. Chem., Anal. Ed., 1, 210 (1929).

Determination of Hydrogen Sulfide in Refinery Still Gases[1]

A. R. Scharnagel and A. W. Trusty

Louisiana Oil Refining Corporation, Shreveport, La.

THE iodine titration method has always been a standard method for the determination of hydrogen sulfide, but with refinery still gases this method is inaccurate because of the reaction of the gaseous unsaturated hydrocarbons with the iodine. The following method has been used in our laboratory: 100 cc. of 0.1 *N* acid lead nitrate is placed in a Fisher gas washing bottle or any convenient scrubber. The gas to be tested is passed through the bottle and metered with a gas meter, or a known volume of water is displaced. A second wash bottle with 100 cc. of 0.1 *N* lead nitrate is placed directly after the first wash bottle. With the slightest discoloration of the second bottle, the rate of flow of the gas is reduced to insure all of the hydrogen sulfide being caught in the first bottle. The second bottle is useful also when testing a gas in which the quantity of hydrogen sulfide is unknown, as the second bottle will be an indicator when the first bottle becomes spent.

The first bottle is filtered, made up to volume, and aliquot portions titrated with ammonium molybdate solution. With convenient factors on the solutions, the method is rapid and accurate.

[1] Received November 3, 1930.

Proposed Modification of Oxygen Consumed Method for Determination of Sea Water Pollution[1]

H. K. Benson and J. F. G. Hicks, Jr.

University of Washington, Seattle, Wash.

By applying the Zimmerman-Reinhardt reaction to alkaline permanganate consumption, an easy and reliable method for the estimation of pollution in sea water is obtained.

Each set of determinations must be calibrated against the blank sample of the purest sea water in the locality of the pollution.

The method may be correlated with other means for the detection of pollution such as the biochemical oxygen demand, bacteria, and plankton.

In using the standard method (*2*) for the determination of pollution in briny waters, considerable difficulty was experienced in this laboratory in obtaining a sharp end point. Also results were not consistent with the known pollution in given samples and the values were several fold too high. Table I shows the variations obtained in samples of sea water from several bays of Puget Sound. These samples were all taken by means of a deep sea tester at a uniform depth of 10 feet. The biochemical oxygen demand was determined after 5 days' incubation in a thermostat at 25° C., and computed to a 20-day basis by use of the sewage factor 0.68.

Table I—Variations in Pollution Data

Sample	B. O. D. *Mg./liter*	Oxygen Consumed by $KMnO_4$ *Mg./liter*	Chlorides *Mg./liter*
1	1.82	18.54	14,750
2	3.49	17.89	14,200
3	0.87	20.29	14,184
4	2.75	17.45	15,905
5	2.21	14.76	15,975
6	4.15	29.34	16,110
7	1.82	13.13	16,075
8	5.88	19.60	15,150

Table II—Comparison of Results by Old and New Methods

Sample	New Method *Mg./liter*	Old Method *Mg./liter*
Blank sea water before incubation		
1	13.0	37.4
2	12.8	46.4
3	12.7	45.0
4	12.5	49.0
5	12.7	40.5
Av.	12.7	43.7
After incubation for 96 hours at 23° C.		
1	6.8	38.3
2	6.7	27.8
3	6.7	28.5
4	7.0	20.2
5	6.8	34.2
Av.	6.8	33.0
Digester liquor dilutions after 96 hours' incubation at 23° C.		
Ratio Liquor to Sea Water		
1:1000	74.5	80.9
	73.8	81.9
1:5000	21.7	40.1
	20.7	23.2
1:10000	14.6	34.3
	13.8	30.8
1:50000	7.2	40.3
	7.2	25.3
Digester liquor dilutions after 24 hours' incubation at 23° C.		
1:7500	25.2	38.2
	25.2	36.2
1:30000	16.1	36.2
	15.9	37.2

It is evident that no correlation exists between the organic content of these samples as measured by the biologic and permanganate oxygen consumptions, respectively. The differences are rather suggestive of slight variations in technic which would permit other reactions than the oxidation of organic matter to proceed. In the presence of iron as a catalyzer it seems probable that the oxidation of the chloride ion by the permanganate ion in acid solution occurs to a variable degree dependent upon time, temperature, and concentration factors. However, at times it was found possible to check aliquot parts of the same sample within 2 or 3 p. p. m. of oxygen by allowing an arbitrary length of time (20 seconds) from the addition of a single drop of permanganate (in back titrating) until the disappearance of its color. Even so, the values obtained for oxygen consumed appear much too large.

In order to enable the accurate reproduction of results in a given sample and to limit the reaction more nearly to the oxidizable organic matter contained in sea water, use is made of the Zimmerman-Reinhardt (*5*) method for the titration of permanganate in the presence of hydrochloric acid.

Proposed Procedure

The digestion is carried out in exactly the same manner as in the standard method (*2*). The modification lies in the determination of unconsumed permanganate. After digestion, the sample is acidified with 25 ml. of the preventative solution containing manganous sulfate, sulfuric acid, and phosphoric acid. Immediately thereafter 10 ml. of standard ferrous sulfate solutions are added. The sample

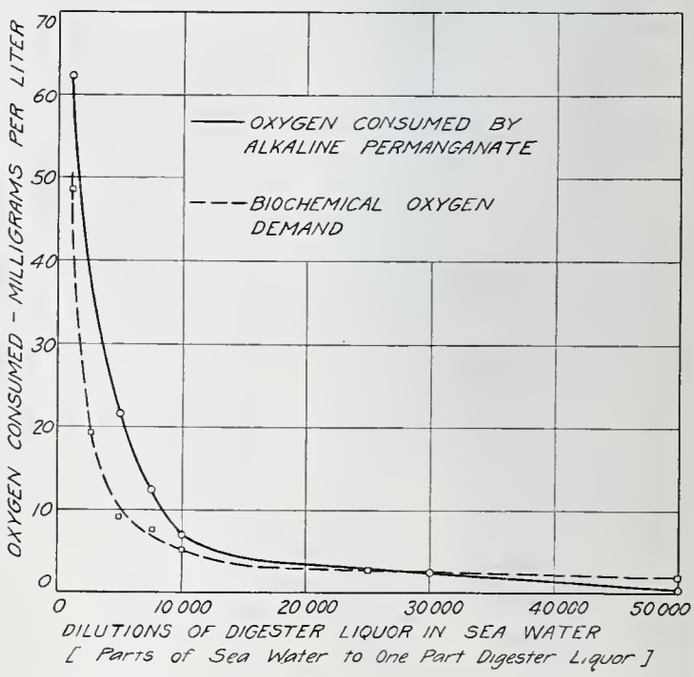


Figure 1

is brought to room temperature and standard permanganate added until the addition of one drop changes the solution from colorless to light pink. This end point is sharp enough so that two identical samples may be checked within 0.02 ml. Tenth normal permanganate standardized against either

[1] Received September 10, 1930.

iron wire or sodium oxalate is used. The iron solution contains ferrous ammonium sulfate and sulfuric acid in concentrations of 0.1 N and 0.3 N, respectively. The preventative solution contained 67 grams of $MnSO_4.4H_2O$, 138 ml. of 85 per cent phosphoric acid, and 130 ml. of sulfuric acid (concd.) diluted to the volume of 1 liter.

The comparison of this method with the standard method is given in the determinations, used in Table II, which utilized various dilutions of waste liquor from sulfite digesters in sea water obtained from Seattle harbor.

With this constancy of results it is obvious that the oxygen-consumed values may be used to indicate the concentrations of sulfite liquor when it is known that it is the polluting agent in sea water. By making up the various dilutions and taking the mean of five determinations on each dilution the results used in Table III were obtained.

Table III—Oxygen Consumed with Sulfite Liquor as Polluting Agent

Dilution of Liquor in Sea Water	Oxygen Consumed by Mixture	Oxygen Consumed by Digester Liquor
	Mg./liter	*Mg./liter*
Blank	11.3	0.0
1:1000	73.7	62.4
1:5000	32.8	21.5
1:7500	23.7	12.4
1:10,000	18.3	7.0
1:30,000	13.7	2.4
1:50,000	11.5	0.2
1:100,000	11.3	0.0

When these values are plotted against concentrations the resulting curve (Figure 1) is either identical or nearly so with that obtained by dividing the 5-day biochemical oxygen demand (*3*) by the sewage factor 0.68 commonly used to express complete biological oxygen consumption. Inasmuch as Rudolfs (*4*) has shown that there is a direct relation between the biochemical oxygen demand, bacteria, and plankton, it would seem that the oxygen consumed as determined by this modified method correlates with the other factors ordinarily used for detection of pollution.

Abbot (*1*) has proposed a modified acid dichromate absorption test as a more sensitive index of oxidizable matter than the permanganate absorption test. His values of the percentage oxidation of various organic substances range from 98 per cent in the case of sodium oxalate to 66 per cent for gelatin. To ascertain the degree of completion of oxidation of organic substances somewhat similar to lignin and the other components of digester liquor, the following compounds were submitted to the modified permanganate consumed test: vanillin, tannic acid, starch, sucrose, and pyrogallol. Complete oxidation is defined according to the following reactions:

Vanillin: $C_8H_8O_3 + 17\ (O) \longrightarrow 8CO_2 + H_2O$
Tannic acid: $C_{14}H_{10}O_9 + 24\ (O) \longrightarrow 14CO_2 + 5H_2O$
Starch: $C_6H_{10}O_5 + 12\ (O) \longrightarrow 6CO_2 + 5H_2O$
Sucrose: $C_{12}H_{22}O_{11} + 24\ (O) \longrightarrow 12CO_2 + 11H_2O$
Pyrogallol: $C_6H_6O_3 + 12\ (O) \longrightarrow 6CO_2 + 3H_2O$

After making correction for the oxygen consumed by the blank, the results given in Table IV were obtained by the modified method.

Table IV—Modified Permanganate Consumed Tests

Substance	Weight of Sample	Oxygen Required Theoretical	Oxygen Required Actual	Complete Oxidation
	Gram	*Gram*	*Gram*	%
Vanillin	0.0159	0.0285	0.0282	99.0
Tannic acid	0.0056	0.0067	0.0044	65.5
Starch	0.0527	0.0626	0.0451	72.0
Sucrose	0.0408	0.0446	0.0372	83.5
Pyrogallol	0.0130	0.0196	0.0152	77.5

From the similarity of these substances to those present in digester liquor it would be reasonable to expect that their oxidation is from 85 to 90 per cent complete.

Literature Cited

(1) Abbot, Ind. Eng. Chem., **19**, 919 (1927).
(2) American Public Health Assocn., "Standard Methods for Examination of Water and Sewage," 6th ed., p. 24, footnote.
(3) Benson, *Paper Trade J.*, **90**, No. 24, 69 (1930).
(4) Rudolfs, Ind. Eng. Chem., **21**, 256 (1929).
(5) Treadwell and Hall, "Analytical Chemistry," Vol. II, pp. 515–8, footnote 2.

Modified Ford-Williams Method[1]

L. H. James

Reo Motor Co., Lansing, Mich.

THE following procedure is applicable to the determination of manganese in high chrome-nickel alloys which are practically insoluble in nitric acid. Such alloys are, however, soluble in nitro-hydrochloric acid.

If either the persulfate or bismuthate method is used for determining the manganese in nickel-chrome alloys soluble only in nitro-hydrochloric acid, it is necessary to remove the hydrochloric acid by fuming with sulfuric acid and the chromium with zinc oxide. The only difficulty encountered in this procedure arises from the fact that the complex sulfates formed often dissolve very slowly after dilution with water. The insolubility of these chromium sulfates probably increases with the temperature and time of fuming, although rather startling variations have been met with in regard to the time required to dissolve the sulfates formed, while working with the same alloy under like conditions.

The Ford-Williams method is the only other practical alternative method used to determine the manganese in such alloys. It is not necessary to separate the chromium in this method, but the hydrochloric acid must be removed by at least two evaporations with nitric acid to a sirupy consistency. Evaporations of this kind are always somewhat troublesome and time-consuming.

The proposed method eliminates the objectionable features of the above-mentioned procedures if the alloy is insoluble in nitric acid, as it is easily carried out, reasonably accurate, and much faster than the methods usually employed. However, if the material to be analyzed is soluble in nitric acid, obviously the following modification cannot be used to any advantage as the Ford-Williams method in its present form has always been recognized as entirely reliable.

Method

Weigh 2 grams of sample into a 500-cc. tall form beaker. Add 15 cc. of hydrochloric acid (sp. gr. 1.19), 5 cc. of nitric acid (sp. gr. 1.42), and 20 cc. of water. Boil until dissolved and add 20 cc. of perchloric acid (60 per cent). Continue to boil until the perchloric acid fumes and insoluble salts start to separate. Cool, dissolve in 30 cc. of nitric acid (sp. gr. 1.42), and heat just to boiling. Add a few crystals of sodium chlorate in order to avoid excessive foaming and then precipitate with four additions of 2 grams each of sodium chlorate adding each portion after the effervescence produced

[1] Received September 3, 1930.

by the last addition has about ceased. This precipitation properly carried out should take about 20 minutes during which time the solution should always be saturated with free chloric acid in order to precipitate the manganese completely. If the solution is overheated at this point, the sodium chlorate decomposes too rapidly and the manganese may not be entirely precipitated. Remove the solution from the hot plate before the effervescence from the last addition of sodium chlorate has entirely ceased, filter on an asbestos pad with suction, and wash thoroughly with water. It is not necessary to allow the solution to cool and settle before filtering although it does no harm. Transfer the pad to the beaker in which the precipitation was made and wash any adhering manganese dioxide from the funnel into the beaker with 100 cc. of water. Dissolve the manganese dioxide in 20 cc. of 0.1 N ferrous sulfate containing 100 cc. of sulfuric acid (sp. gr. 1.84) per liter, and titrate back to a permanent pink end point with 0.1 N potassium permanganate.

Calculate the manganese by means of the following formula:

$$\text{Per cent Mn} = \frac{[(A \times B) - C] \times 0.2747 \times D}{\text{Weight of sample}}$$

A = cc. of 0.1 N ferrous sulfate
B = permanganate solution equivalent of the 0.1 N sulfate
C = cc. of 0.1 N potassium permanganate
D = normality factor of 0.1 N potassium permanganate

In order to estimate the accuracy of this method, the manganese in two stainless steels containing approximately 1.5 per cent silicon, 8 per cent chromium, and 22 per cent nickel, was carefully determined by both the persulfate and bismuthate methods, after separating the chromium with zinc oxide. The average percentage obtained from four determinations on each steel was assumed to be the correct manganese content of these two samples which are designated in the table as 1 and 2.

Determination of Manganese in Eight Samples

Sample	Manganese Obtained					Manganese Present
	1	2	3	4	Av.	
	%	%	%	%	%	%
1	0.85	0.81	0.81	0.83	0.83	0.83
2	0.49	0.50	0.49	0.51	0.50	0.51
12*c*	0.41	0.39	0.38	0.43	0.40	0.409
72	0.64	0.64	0.65	0.62	0.64	0.651
32*a*	0.25	0.24	0.25	0.24	0.25	0.244
30*b*	0.49	0.48	0.48	0.50	0.49	0.499
10*c*	1.12	1.15	1.14	1.13	1.14	1.13
7*a*	0.42	0.41	0.42	0.42	0.42	0.446

The manganese in five Bureau of Standards standard steel samples and one iron (7*a*) was also determined and included in this table in order to compare further the accuracy of the above method with the commonly used procedures. The results on iron (7*a*) were obtained without separating the silicon or graphitic carbon.

Four determinations on each sample were run at the same time without employing any more care or refined apparatus than is ordinarily used to obtain reasonably accurate results in routine steel work. The theoretical titer was used as shown in the preceding formula to calculate the results thus obtained, which were tabulated without rejecting the percentages obviously inaccurate. These values, however, considered as a whole would be closer to the theoretical percentages if multiplied by 1.02 as an empirical factor.

Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium[1]

Wilfred W. Scott and Samuel M. Alldredge

University of Southern California, Los Angeles, Calif.

A METHOD commonly given by standard texts upon quantitative chemical analyses for separating lead from barium and calcium depends upon the solubility of lead sulfate and the insolubility of barium and calcium sulfates in ammonium acetate solution. It is the intention of this piece of work to test out that method as regards its completeness of separation.

Previous Investigations

In speaking of the precipitation of lead as a sulfate in the determination of lead in ores and metallurgical products, Treadwell and Hall (*7*) claim that the precipitate of lead sulfate containing silica and barium sulfate (also strontium and sometimes calcium sulfate) can be purified by redissolving the lead in hot ammonium acetate solution. They suggest that the lead extraction be made with 20 cc. of hot 2 N ammonium acetate.

Low (*2*) suggests the use of ammonium or sodium acetate solution in dissolving lead sulfate. He would titrate the lead solution with standard ammonium molybdate solution while the calcium remains out of solution.

In the analysis of fluorspar Sisco (*6*) claims that lead and barium sulfates are separated by the acetate extraction using a 20 per cent solution of ammonium acetate.

Scott (*5*) considers the barium sulfate slightly soluble in ammonium acetate and hence a possible contaminant of the extracted lead.

The problem has two main parts—namely, (1) is barium extracted with the lead; and (2) is calcium extracted with the lead when ammonium acetate, hot and concentrated, is used upon a precipitated mixture of the sulfates of lead, barium, and calcium?

A subdivision of the problem, however, of minor importance was added by the claim of Majdel (*3*) that the separation of lead from barium in the presence of barium, by precipitating both components with sulfuric acid and dissolving lead sulfate in ammonium acetate, is not possible as the double salt of lead and barium sulfate is formed which is insoluble in ammonium acetate, and, therefore, a part of the lead remains with barium. The error is greater as the ratio of barium to lead increases. In proportion of Pb:Ba as 1:0.6, 9 per cent lead remains in the undissolved barium sulfate; as 1:1, 45 per cent; as 1:2, 88 per cent; as 1:7, 100 per cent; and is thereby lost. The separation must be accomplished, therefore, with hydrogen sulfide.

The ratio of 1 lead to 100 barium was taken. The precipitated mixture of their sulfates was extracted ten times with boiling 50 per cent ammonium acetate as given below. The filter and its residue then were boiled with 100 cc. of 50 per cent ammonium acetate until spattering commenced. Fifty cubic centimeters more of ammonium acetate were added, the mixture heated to boiling and allowed to settle.

[1] Received August 12, 1930.

Experimental Data

Determination	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
Solution of ammonium acetate, per cent	50	50	50	50	50	50	50	50	25	25	50	Hot water	Hot water	50	50
Number of extractions made	6	6	6	6	8	8	8	8	8	8	12	8	8	8	8
Volume used in each extraction, cc.	25	25	25	25	25	25	25	25	25	25	30	25	25	25	25
Lead in sample, gram	0.0200	0.0200	0.0200	0.0200	0.0200	0.0200	00.020	0.0200	0.0200	0.0200	0.0100	....	....	....	....
Lead in extract, gram	0.0199	0.0200	0.0199	0.0199	0.0199	0.0198	0.0198	0.0199	0.0198	0.0198	0.0095	....	....	....	....
Lead extracted, per cent	99.5	100	99.5	99.5	99.5	99.0	99.0	99.5	99.0	99.0	95.0	....	....	....	....
Barium in sample, gram	0.0100	0.0100	0.0200	0.0200	0.0800	0.0800	0.0900	0.0900	0.0600	0.0600	1.000	....	....	....	....
Barium extracted	None	None	None	None	None	None	None	None	None	None	....	....	....	....	....
Calcium in sample, gram	0.0100	0.0100	0.0200	0.0200	0.0800	0.0800	0.0900	0.0900	0.0600	0.0600	None	0.0600	0.0600	0.0600	0.0600
Calcium extracted, per cent	....	....	....	....	3.37	3.62	0.66	0.77	8.50	5.00	....	26.3	35.3	3.16	19.5

It was then filtered, the filtrate being passed into the filtrate of the first ten extractions. The results of this extraction may be found under column 11 of the data.

In all extractions the filter paper with its precipitated sulfates was transferred to a casserole, 25 cc. of concentrated ammonium acetate added, and heated to boiling. The acetate solution was filtered through a Swedish filter paper. This was repeated six or eight times until the paper in the casserole and funnel did not darken when touched with a rod containing a drop of hydrogen sulfide solution. The filter paper in the funnel was washed four times with hot water and squeezed well to remove all liquid.

Method of Procedure

Known mixtures of lead nitrate, barium nitrate, and calcium carbonate are dissolved in water acidulated with nitric acid. An excess of sulfuric acid is added to the mixture and taken to sulfuric acid fumes. This is cooled, diluted, filtered on Swedish filter paper, and washed well with water containing 10 per cent sulfuric acid. The filter paper with its residue is placed in a casserole and extracted with 30 cc. of hot, concentrated ammonium acetate, and the solution decanted through filter paper. This extraction is repeated until the filtrate indicates no lead when a drop of the filtrate is put in some potassium chromate solution. It requires about six to eight extractions to get negative tests for lead on the filtrate.

Filtrate I. This contains the lead and possibly some of the barium and calcium. The filtrate is made faintly acid with hydrochloric acid and hydrogen sulfide is passed through it for 30 minutes. It is then heated on a steam bath for same period of time and filtered.

Filtrate II. Contains barium and calcium. This filtrate is evaporated nearly to dryness and the sulfides dissolved in the least amount of hydrochloric acid, and the excess acid expelled by evaporation. The residue is taken up in 300 cc. of water containing 5 drops of acetic acid. Sufficient ammonium acetate solution is added to make the solution neutral. An excess of potassium chromate solution is added after heating the solution to boiling. The solution is allowed to settle until cold. It is filtered through a Gooch crucible.

Filtrate III. Contains calcium. To the neutral solution after heating to boiling, 10 cc. of acetic acid are added and 15 cc. of a saturated solution of oxalic acid, and after 5 minutes, a slight excess of ammonia. It is allowed to cool an hour, then decanted through a filter. The precipitate is ignited wet in a weighed crucible and strongly heated to constant weight. It is weighed as calcium oxide.

Residue I. Contains most of the barium and calcium. This was discarded in this problem.

Residue II. Contains the lead as a sulfide. This residue is washed well with water saturated with hydrogen sulfide gas. It is then treated with hot hydrochloric acid and then nitric acid and heated to boiling. Ten cubic centimeters of concentrated sulfuric acid are added and the solution evaporated to strong sulfuric acid fumes. It is cooled, diluted with water, and filtered on an asbestos mat in a weighed Gooch crucible. The residue is washed with dilute sulfuric acid and with alcohol, and dried at a dull red heat. It is weighed as lead sulfate.

Residue III. Contains barium as a chromate. It is washed with a dilute potassium chromate solution until free of calcium and with water until free of potassium chromate. It is then washed once with dilute alcohol, dried at 110° C., and weighed as barium chromate.

Results

The data of the first ten columns (of the table of experimental data) are the result of twenty-two determinations on lead. If the lead did not check with the amount in the original sample, the sample was discarded and another one begun. In case the amount of lead sulfate ran high, further heating sometimes brought the amount of lead down to the amount in the sample. The general tendency, however, was for the lead to run low. The work was done with extreme care. Each sample was weighed separately and carefully. Considering the slight solubility of lead sulfate and the small amount of lead in the sample, a slight loss of lead is to be expected, as is shown in the table.

Outstanding Findings of the Work

(1) In a ratio of calcium to barium of 1 to 1: (*a*) all lead is extracted, (*b*) no barium is extracted, (*c*) as much as 8.5 per cent of calcium is extracted.

(2) In a ratio of calcium to barium of 1 to 9.3, no barium is extracted.

(3) In a ratio of lead to barium of 1 to 100, 95 per cent of lead is extracted.

Conclusions

(1) Lead may be separated from barium by ammonium acetate extraction of their sulfates, the barium not passing into the lead solution in appreciable amounts.

(2) Lead cannot be separated entirely from calcium by ammonium acetate extraction, the calcium passing into the lead solution in considerable quantity.

(3) The amount of calcium passing into the lead solution seems to depend upon certain physical factors not in control of the operator. The writers suggest these as possible factors: the time required in filtering each extract, the amount of cooling during filtration, small changes in the density of the acetate solution during boiling.

(4) As the amount of barium is increased there seems to be an increasing difficulty in extracting all the lead. This may be due to physical occlusion of the lead sulfate by the barium sulfate or to the formation of a definite lead-barium salt which is insoluble. The writers are inclined to believe from the data in column 11 of the table that this noticeable difficulty may be due to occlusion.

(5) Less calcium is extracted in the presence of lead and barium than when it is the only constituent of the sulfate precipitate.

Literature Cited

(1) Hillebrand and Lundell, "Quantitative Analysis," Wiley, New York, 1929.

(2) Low, "Technical Methods of Ore Analysis," Wiley, New York, 1927.

(3) Majdel, *Art. hem. farm.*, **4**, 76–8 (1930).

(4) Olsen, "Quantitative Chemical Analysis," Van Nostrand, New York, 1926.

(5) Scott, "Standard Methods of Chemical Analysis," Vol. I, Van Nostrand, New York, 1925.

(6) Sisco, "Technical Analysis of Steel and Steel Works Material," McGraw-Hill, New York, 1923.

(7) Treadwell and Hall, "Quantitative Analysis," Vol. II, Wiley, New York, 1919.

Measurement of Drillability of Fertilizers[1]

Arnon L. Mehring

Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

The drillability of a fertilizer affects its flow from most distributors in two ways: It determines (1) the quantity of fertilizer that will be applied on any given field with a fixed setting of the mechanism, and (2) the degree of uniformity or quality of its distribution. The comparative rate of flow of a fertilizer under a given force may be determined if its angle of repose, apparent specific gravity, and average particle diameter are known. Of these the angle of repose is of greatest and particle size of least importance. Under the conditions prevailing in the field application of ordinary fertilizer the effect of particle size is often negligible. The angle of repose of a fertilizer is also an indication of the degree of uniformity attainable with distributors in its application to crops. Directions are outlined for measuring the angle of repose, apparent specific gravity, and average particle diameter of fertilizers. A method is given by which a coefficient of the rate of flow of the fertilizer may be obtained by substituting these three measurements in an equation.

THE term drillability is used to denote the resultant of all the properties of fertilizers that affect the manner in which they flow. The properties and therefore the drillabilities of different fertilizers vary widely and the drillability of even the same fertilizer is apt to change from time to time with variations in external conditions (*4*). The drillability of a fertilizer affects its flow from most distributors in two ways: It determines (1) the quantity of fertilizer that will be applied on any given field with a fixed setting of the mechanism, and (2) the degree of uniformity or quality of its distribution.

For maximum efficiency fertilizers must be applied uniformly (*1*) and at the proper rate. These conditions are difficult, if not impossible, to obtain at present. A method of measuring drillability would facilitate obtaining desired rates of application and thus lead to greater efficiency in the use of fertilizers.

With a little experience good and poor drillability in a fertilizer can be distinguished just as readily as hot and cold weather, but small differences in drillability like small differences in temperature and humidity can only be detected by instruments.

A search of the literature has revealed only one method (*3*) for measuring drillability. This was devised by Doctor Wichern in Germany and is intended only for superphosphates. The apparatus used is shown in Figure 1. To make a determination, 25 grams of superphosphate previously passed through a 2-mm. sieve are placed in each bowl and 10 glass marbles, weighing exactly 100 grams, are placed on top of each sample. The reciprocating motion of the apparatus causes the marbles to roll back and forth until they finally pack the fertilizer into a cake which will not fall from the bowl when it is inverted. The time required to do this is used as the measure of the drillability of the superphosphate.

This apparatus distinguishes between superphosphates of satisfactory and unsatisfactory drillability and assigns numerical values to the drillability which is very desirable. It will not, however, work satisfactorily with certain kinds of fertilizers, nor give a numerical value that can be relied upon with superphosphates of the best drillability. Three samples tested by it in this laboratory showed no signs of packing after one hour although all the conditions laid down for the test were rigorously met. They did pack down, however, after still longer periods of time. The drillability of a fertilizer depends to a large extent upon its content of moisture and very fine particles. These also determine the length of time required to pack the sample in the apparatus, but under the conditions of this test both the moisture and fine powder content are apt to change very greatly during the test. The amount of exposure to the air in the screening, weighing, and shaking is so great in proportion to the size of the sample that unless already approximately in equilibrium with the atmosphere, its moisture content is bound to change. Thus the length of time required to pack the sample may depend upon the relative humidity of the atmosphere much more than upon the condition of the material being tested. The amount of fine powder in the sample is usually increased during the determination because the marbles have much the same effect as the balls in a ball mill. Thus a granular superphosphate may be reduced to an impalpable powder in this apparatus and when this occurs the sample will pack tightly, although it would not pack tightly so long as it remained in a granular condition. The length of time required for packing depends upon the original size and hardness of the particles, which may or may not affect the drillability.

To be of greatest value a method of measuring drillability should apply to all kinds of fertilizers and over the entire range of drillability, give reliable results that can be duplicated, be easily and quickly carried out, and not involve the use of equipment that is expensive or difficult to procure. This paper gives a method for measuring the drillability of fertilizers which promises to meet these requirements.

Theoretical Considerations

Drillability consists of two elements, the rate of flow (unit of mass per unit of time) through a fixed opening, and the degree of uniformity of flow when subjected to a given amount of force. This force in all fertilizer distributors except the top delivery type consists of two components in varying proportions according to the type of mechanism. These components are the pressure supplied by the dispensing mechanism and the force of gravity.

In the top delivery type the rate of delivery is independent of the force of gravity, and thus all fertilizers are delivered at the same rate when calculated on a volume basis. Application rates, however, are computed by weight per unit of area, and on this basis rates by the top delivery type of distributor vary with the apparent specific gravity of the fertilizer. There is no flow in the hopper of the top delivery type and therefore the rate of delivery on a weight basis can be determined if only the apparent specific gravity of the fertilizer is known.

The vast majority of distributors now in use deliver the fertilizer from an orifice at the bottom of the hopper. With this type the fertilizer flows to the delivery opening and the

[1] Received October 9, 1930. Presented before the Division of Fertilizer Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

delivery rate with a given setting of the quantity-regulating devices depends upon the angle of repose, apparent specific gravity, and average diameter of the particles composing the mass.

The kinetic angle of repose is the slope which a substance forms with the horizontal when it has come to rest after being carefully poured into a pile. It measures the point at which the forces tending to continue the flow exactly balance the forces opposing the flow, or in other words, the friction between the particles. The effect of cohesion caused by the presence of moisture and of very small particles, and part of the effect of specific gravity on the rate of flow also affect the angle of repose. The rate of flow of comminuted solids and consequently the delivery rate of fertilizers by most distributors varies inversely with the angle of repose. No flow from an orifice can be caused by gravity alone when the kinetic angle of repose is greater than 45 degrees, but fertilizer distributors in operation exert pressure upon the material being dispensed by means of paddle wheels, revolving plates, or other devices. This pressure increases the rate of flow and thus many distributors can dispense materials with angles of repose considerably higher than 45 degrees.

Figure 1—Wichern Apparatus for Measuring Drillability of Superphosphates

Rate of flow varies directly with the apparent specific gravity. With most fertilizer distributors the variations in rate of delivery caused by differences in apparent specific gravities are less than those caused by differences in the angles of repose.

Average particle size is not an appreciable factor in the rate of flow of materials when they are not in a confined space, as, for example, when poured from a vessel or flowing down an inclined chute. It becomes important when the flow is in a confined space and the diameter of the particles approaches in size that of the opening through which they flow. Most materials fail to flow through an opening with a diameter less than 5 times the average diameter of its particles. Under field conditions the effect of size of the particles of the fertilizer on rate of delivery is often negligible.

The second element of drillability is the degree of uniformity of distribution. Irregular distribution of a homogeneous fertilizer is caused, first, by the fact that cohesion of the particles of the mass is greater than the forces available for separating them, and second, by various mechanical imperfections in the distributor. The irregularities caused by cohesion may be measured by the angle of repose of the material.

Measurements of the temperature, relative humidity, and wind velocity of the atmosphere are each important in interpreting the weather, but no simple means exists for measuring the effect of all these simultaneously so that a single figure will answer for all purposes. Drillability, like the weather, cannot be completely measured by a single determination, because it is composed of two elements. These, as explained before, are the rate of flow and degree of uniformity of flow.

Measurement of Rate of Flow

The factors that affect the rate of flow of a subdivided solid are the coefficient of friction, apparent density, and size of the particles composing the mass. Rates of flow of fertilizers that have low angles of repose may be determined directly by measuring with a stop-watch the time required for a definite weight of material to flow by gravity from a specially constructed funnel. Many fertilizers now in use, however, will not flow by gravity alone so that this method is of limited usefulness. Although a machine could be devised to exert constant pressure upon them and thus cause most materials to flow, yet certain of the materials that flow well by gravity alone do not flow at all when subjected to pressure in such a machine. The material is crushed or the machine is broken. The only method so far known that will apply to all fertilizer materials and mixtures is the use of a formula, requiring measurements of the angle of repose, the average particle diameter, and the apparent density of the fertilizer.

In a previous study (*2*) of the flow of masses of solid particles as the result of the force of gravity the following formula was derived:

$$t = \frac{\mu}{B^{5/2}d}\,[34.6 + (67.4 + 444 \sin {}^1/_2\,\phi)\,(D/B + 0.130 - 0.161\mu)] \quad (1)$$

where t is the time in minutes required for 100 grams to flow through an orifice, μ is the kinetic coefficient of friction or natural tangent of the angle of repose, B is the diameter of the orifice in millimeters, d is the apparent specific gravity of the material, ϕ is the vertical angle of the hopper bottom, and D the average diameter of the particles in millimeters. The rates of flow calculated for various materials by use of this equation agreed remarkably well with experimentally determined rates. The materials included a number of fertilizers, sand, lead shot, various seeds, marbles, etc., and thus embraced a wide range of physical properties. The variation between the calculated and observed time required for a given weight of any material to flow was no greater than the experimental errors involved in determining the time and it is therefore concluded that measurements of the angle of repose, apparent specific gravity, and average particle size are sufficient to determine completely the comparative rate of flow of a fertilizer.

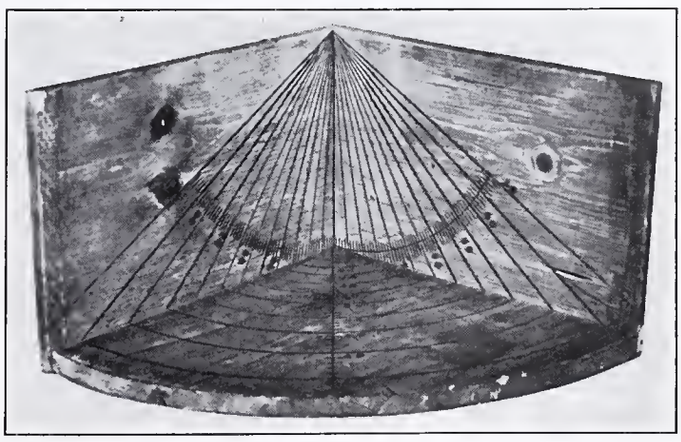


Figure 2—Easily Constructed and Convenient Apparatus for Measuring Angle of Repose of Fertilizers

Although Equation 1 gives excellent results for materials that flow by gravity, it does not hold good for those that re-

quire pressure to flow. Empirical Equation 2, however, appears to be satisfactory for all fertilizers.

$$t = \frac{\mu}{B^{5/2}d}\left[34.6 + (67.4 + 444 \sin {}^1/_2\phi)\left(D/B + \frac{0.005}{\mu^3}\right)\right] \quad (2)$$

For all materials that will flow by gravity t is the actual time consumed. Although t is a hypothetical figure when measurements of a material that will not flow by gravity are substituted in the equation, it nevertheless has a value corresponding to the delivery rates actually given by distributors.

Figure 3—Proper Position of Pouring Vessel in Relation to Apex of Cone

The values of t may be used as coefficients of rate of flow if arbitrary values are assigned to B and ϕ. If this is done the same values should be used by all who employ the method so that the results of one worker may be compared with those of others. For this purpose $B = 15$ and $\phi = 60$ degrees seem reasonable since these figures represent about average conditions found in the use of fertilizer distributors. Other values might answer equally well. t in Equations 1 and 2 was the time in minutes required by 100 grams to flow. When the above values are substituted in the Equation, t is generally a fraction with a zero in the first decimal place. It would therefore be more convenient to change the formula so as to obtain T, the time necessary for 1 kg. of fertilizer to flow. By making these changes we get Equation 3.

$$T = \frac{\mu}{87.146\, d}\left[34.6 + 289.4\left(\frac{D}{15} + \frac{0.005}{\mu^3}\right)\right] \quad (3)$$

T may be considered as a coefficient of rate of flow. Detailed instructions for obtaining the values of μ, d, and D follow.

Measurement of Angle of Repose—A method employing a simple and convenient device, illustrated in Figure 2, has been used for a number of years in the Bureau of Chemistry and Soils (*4*) for making kinetic angle of repose measurements where an accuracy of ± 0.5 degree was sufficient.

For more accurate work the following method may be used: The sample should be measured preferably in the same room in which it has been stored, since it is apt to be more nearly in equilibrium with this than with some other atmosphere. About 5 pounds is a convenient amount to measure but it need not be weighed, since after taking the sample no time should be lost in making the determination. About three-fourths of the sample should be rapidly but carefully poured into a conical heap upon a rigid and approximately level surface, such as a table, placed out of all drafts or air currents. The balance of the material must be poured slowly and very carefully. The final pouring may be done from an Erlenmeyer flask or cylinder held as shown in Figure 3, and slowly rotated so that a very thin stream of material will fall from a distance of no greater than 5 mm. directly upon the apex of the cone. If the pouring is too fast or from too great a height the velocity acquired by the particles will reduce the slope of the pile and the resulting determination will be too low. The pile must not be touched or jarred in any way. If this does occur accidentally more material may be added to the pile until the effects of the disturbance are obliterated. With a few fertilizers the pile will build up rapidly and then slump down followed by a repetition of these events in a cyclic manner. When this occurs the cone should be measured as nearly as possible at its highest point in the cycle. The apex of the cone should be as sharp as possible. The height of this pile divided by the average radius of its base is the coefficient of friction of the material, μ, or the tangent of its angle of repose. From this value the angle of repose may be found in a table of natural tangents. It may also be measured directly with a protractor level such as is commonly used by machinists and carpenters. The face of the instrument shown in Figure 4 was extended for greater accuracy by attaching a strip of metal to it. To make a measurement the limb of the protractor should be clamped in a level position in a ring stand. The face of the protractor should then be made to coincide in direction with the slope of the cone in the manner shown in Figure 5, but care must be used that it does not touch the pile. The angle of repose is then read off from the scale on the instrument. If the material is homogeneous and the pouring has been properly done, the angle will be the same wherever it is measured. On the other hand, heterogeneous mixtures will give variable angles and a sufficient number of measurements on different parts of the pile must be made and averaged to secure a true mean value. In every case at least four readings should be averaged for a determination.

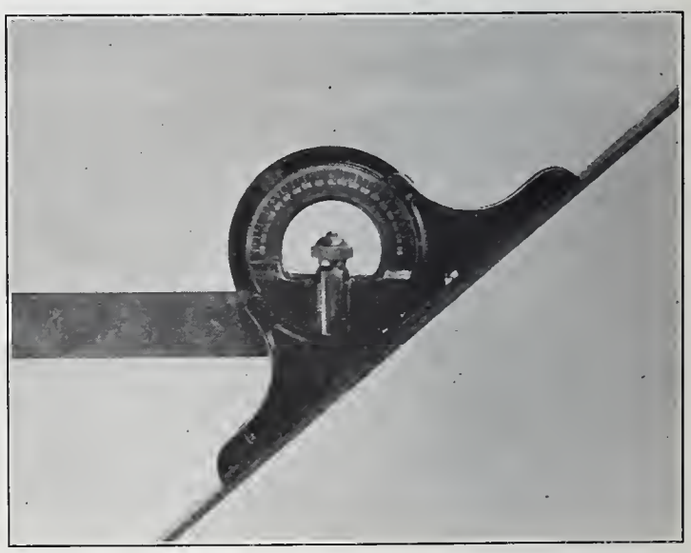


Figure 4—Protractor Level Used for Measuring Angle of Repose of Fertilizers. The Face Was Extended by Screwing a Strip of Metal to It

Mixtures containing particles varying in size and specific gravity when poured into a pile in the manner described above sometimes produce cones with dished sides, as shown in Figure 6. The slope is steeper near the apex than it is near the base. Large round particles also may roll beyond the real base of the cone. The proper slope to measure is that of a line connecting the apex and any point in the circumference of the base.

Duplicate readings made as above on materials with

angles of repose up to 45 degrees made by different operators or the same operator at different times on the same material should agree to within 0.5 degree. The degree of accuracy varies with the size of the pile measured as shown by Table I. The angle of repose becomes increasingly difficult to measure accurately as its value is raised above 45 degrees although approximate measurements may be made up to values of about 65 degrees. For practical purposes it is usually sufficient to know the angle of repose to the closest whole number. With some distributors it is impossible to secure satisfactory distribution of materials with angles of repose of 55 degrees or above. The minimum value for a fertilizer material encountered in this laboratory is 22 degrees. The average mixed fertilizer when measured in the manner described above has an angle of about 40 degrees.

Table I—Effect of Size of Sample upon Accuracy of Angle of Repose Measurements

Weight of Sample	Measurement by First Operator	Measurement by Second Operator
Pounds	*Degrees*	*Degrees*
1	34.6	34.1
5	34.5	34.3
25	34.31	34.37
200	34.39	34.37
2000	34.380	34.375

Measurement of Apparent Specific Gravity—The apparent specific gravity is the weight of a unit volume of the material. It is measured in connection with the testing of various classes of materials, either with or without tamping. Since fertilizers are never tamped down in the hopper of a distributor but on the contrary are often kept in a loose uncompacted condition by the agitator of the distributor it is felt that for fertilizers this measure will be of greatest value if the material is not compressed. The following procedure has been found satisfactory: Fill a 100-cc. graduated cylinder to the 50-cc. mark and lightly tap the bottom of the cylinder on the palm of the hand three times. Then fill to the 100-cc. mark and tap three times more. Refill to

Figure 5—Manner of Making Angle of Repose Measurements with Protractor Level

the mark and tap as before until the material does not settle further with light tapping. The weight in grams of the contents of the cylinder divided by 100 is the apparent specific gravity. To be comparable this determination must always be made in the same manner.

Measurement of Average Particle Size—When the particles composing a mass are all or nearly all of the same relative size, the average diameter may be quickly determined by screening and use of the equation $D = {}^1/_2\,(D_1 + D_2)$ where D is the average diameter of the particles, D_1 is the diameter of the openings in a screen through which the bulk of the material will pass, and D_2 is the diameter of the openings in a screen which will hold it.

Figure 6—Irregular Slopes Obtained with Heterogeneous Mixtures

It requires the exercise of judgment to determine the correct angle of repose in such cases.

Commercial fertilizers are usually composed of particles widely varying in size. Under these circumstances the rate of flow will be different from that of a material composed of uniformly sized particles and a set of sieves or screens should be used in which the size of the openings form a series in which each member is about one-half the value of the preceding. The effective size may then be calculated by use of the equation

$$D = 0.8\,\frac{(D^5_1 - D^5_2)P_1 + (D^5_2 - D^5_3)P_2 + (D^5_3 - D^5_4)P_3 + \ldots}{(D^4_1 - D^4_2)P_1 + (D^4_2 - D^4_3)P_2 + (D^4_3 - D^4_4)P_3 + \ldots} \quad (4)$$

where D_1, D_2, D_3. . . are the diameters of the sieve openings, and P_1, P_2, P_3. . . are the percentages of material found in the indicated intervals. Less than 5 per cent of any of the sizes may be omitted from the calculation without any material effect upon the result. When the effective particle size is determined in this way its value is equal to that necessary, in a mass composed entirely of particles with uniform diameters, to flow at the same rate.

Measurement of Degree of Uniformity of Flow

In a previous study (*4*) the relation between the angles of repose of fertilizers and the degree of uniformity of flow was determined by collecting the amount of fertilizer deposited in each foot of row and calculating the average deviations from the mean rate of delivery. These deviations were complicated by variations in delivery caused by the machines, but this work coupled with numerous other observations of distributors in action shows that the angle of repose gives a good indication of the degree of uniformity of distribution attainable with ordinary distributors. Directions for making this determination have already been given in connection with the measurement of the comparative rate of flow. The same determination will answer for both purposes.

When the angle of repose is less than 40 degrees, cohesion is imperceptible and any homogeneous fertilizer with an angle of repose below this value will flow uniformly if the forces applied to it remain constant. When in practice they do not, it is because of imperfections of the distributor.

As the angle of repose of a fertilizer increases above 45 degrees it flows more and more irregularly. With most distributors the degree of irregularity of distribution increases at a more rapid rate than the angle of repose until finally a point is reached at which flow ceases altogether.

Discussion

Whether more than one or all of the measurements outlined above should be made in any particular case must depend upon the circumstances and the purpose in view. If a complete statement of the drillability of a fertilizer is desired in mathematical terms, the angle of repose, apparent density, and average particle diameter should be measured and T computed by substitution of the proper terms in Equation 3. All four values should be reported. In the case of distributors depending largely upon gravity for the flow of the fertilizer, T will be inversely proportional to the rates of delivery at each adjustment of the mechanism and this holds good for all fertilizers, not merely for commercial mixtures with average properties. These distributors constitute a large proportion of those now in use. In the proportion that the delivery of the fertilizer is effected by mechanical force, the apparent density will determine the delivery rate. Delivery is brought about entirely by the pressure supplied by the mechanism of the top delivery type and largely so by that of the auger type. In every case the angle of repose will indicate the degree of uniformity of distribution likely to be obtained independently of that caused directly by the machine.

The ratio of the average particle diameter of the majority of commercial mixed goods to the size of the delivery opening of the ordinary distributor when making average applications remains approximately constant. Therefore the delivery rates of such mixtures can be determined, if suitable standard calibrations of the implement are available, from the angle of repose and apparent density only.

For some purposes the angle of repose measurement alone will be satisfactory as a rough measure both of rate of flow and degree of uniformity of flow; for example, when several samples of the same kind of material are compared, since they are likely to have nearly the same apparent densities, or when measurements are made at different times upon the same fertilizer. Variations in the apparent specific gravity of more than ± 0.1, however, must not be neglected even in rough work.

In comparing the effects of different fertilizer formulas or of various sources of a single fertilizing element upon crops in the field it is important that each plot should be fertilized with the same degree of uniformity and at the proper rate. It has been difficult to do this with machinery in the past. The use of the measurements outlined above will give control of the drillability of the fertilizer and should assist in getting better results from such agronomic experiments.

Drillability measurements may also be used by implement manufacturers to calibrate distributors more accurately, by fertilizer manufacturers to standardize their products and to maintain uniform drillability, and in other ways.

Acknowledgment

Credit is due W. E. Deming, associate mathematician of this division, for assistance in deriving the formulas in this work.

Literature Cited

(1) Cumings, Mehring, and Sachs, *Agr. Eng.*, **11**, 149–60 (1930).
(2) Deming and Mehring, Ind. Eng. Chem., **21**, 661 (1929).
(3) Dreyspring and Krügel, International Union of Superphosphate Mfrs., *Gen. Circ.* **42**, February 17, 1930; *Superphosphate*, **3**, 157–9 (1930).
(4) Mehring and Cumings, U. S. Dept. Agr., *Tech. Bull.* **182** (1930).

Conductometric Formula for Determining Ash in Both Raw and Refinery Sirups and Molasses[1]

Louis Sattler and F. W. Zerban

N. Y. Sugar Trade Laboratory, 80 South St., New York, N. Y.

A conductometric method has been provided for the determination of ash in both raw and refinery sirups and molasses. It is applicable to those products regardless of their geographical source or their factory and refinery treatment.

In previous papers the writers have pointed out the difficulties entailed in attempting to predict the per cent ash in raw sugars from the electrical conductivity of their solutions. The crux of the problem lay in the variability of the chemical composition of the conducting substances. This variability was found to be considerable in samples which came even from the same district, and so larger variations in the ratio of ash divided by conductance—that is, the C-ratio—were to be expected for different geographical sources.

In those cases where the C-ratio was found to vary within narrow limits, an average ratio was all that was necessary in order to determine the per cent ash in a given sample. The specific conductance of the solution containing 5 grams of raw sugar in 100 ml. was multiplied by the specific C-ratio of the particular community, and the ash was thus at once obtained (*1*).

When the origin of the sugar was unknown, the simple conductance method was inadequate, and it was shown (*2*) that the equation

$$\text{Ash} = 0.001757(0.913\,K + 193.5 - 0.1\,K_1) \quad (1)$$

gave good results regardless of the source of the sugar. Here K is the simple conductance $\times 10^6$ as mentioned before, and K_1 is the specific conductance $\times 10^6$ of a solution made by taking 200 ml. of a sugar solution (5 grams per 100 ml.) and adding to it 5 ml. of 0.25 N hydrochloric acid.

When the above method was applied to other sugar products, Formula 1, with the factor in it multiplied by 10, was found to hold under specific experimental conditions (0.5 gram product plus 4.5 grams sucrose in 100 ml.) for sirups and molasses produced in the raw cane sugar factory, but it did not give good results for refinery sirups (*3*). The factor in the equation was lower than 0.01757 for final refinery sirups, lower still for unfiltered sirups and still lower for filtered sirups. Not only that, but the factor varied from refinery to refinery, and so the simple conductometric Formula 1 was found to be quite unsatisfactory. Obviously the difficulties due to the variability in the chemi-

[1] Received September 18, 1930. Presented before the Division of Sugar Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

cal composition of the conducting substances were aggravated by the treatment in the refinery. It was apparent that the decrease in the value of the factor kept pace with the increase in the extent of the bone black treatment. This was experimentally verified (*4*), and the conclusion was drawn that the results could be accounted for by the selective adsorption of cations as well as of anions by the bone black.

Conductometric studies with 0.25 N potassium hydroxide instead of 0.25 N hydrochloric acid were made on the 175 remaining samples in the hope that some information might be secured regarding the nature of the cations in the various types of sugar products under investigation. This equation was developed:

$$\text{Per cent ash} = 0.01757(1.33\,K + 498.3 - 0.091\,K_1 - 0.5\,K_2) \quad (2)$$

where K and K_1 are the specific conductances $\times 10^6$ without and with 0.25 N hydrochloric acid, respectively, and K_2 is the specific conductance $\times 10^6$ with 0.25 N potassium hydroxide.

Although the formula gave excellent results with refinery products, it was exceedingly poor for Porto Rican blackstraps. The equation was not at all as general as had been desired, and so the problem was attacked from a slightly different angle.

Orthophosphoric acid is only a moderately strong acid, and it could be expected to do two things—to displace the weak organic acids which were present as salts, and to react with the di- and tri-valent metallic ions. The use of this acid in place of the hydrochloric acid has apparently solved the general problem of ash determination, and the present paper provides a method which is applicable to various cane sirups and molasses regardless of their geographical source or their factory and refinery treatment.

The range in the per cent ash in the products studied varied between 4.84 and 14.23 per cent, and for the 133 samples which were still available for the conductometric determinations with phosphoric acid, the maximum deviation between chemical ash and ash calculated from the conductivity measurements was ±0.30 per cent compared to 1 per cent when Formula 2 was used. With an average chemical ash of 9.209 per cent the average deviation of the conductometric ash was found to be ±0.134 per cent for the entire series taken as a supposedly homogeneous group.

Method

The experimental procedure was, in general, the same as in the determinations made previously with hydrochloric acid. Duplicate ash determinations were made in silica dishes on samples which had been filtered by suction through a mat of filter paper pulp covered with asbestos. The important change consists in the addition of 5 ml. of normal orthophosphoric acid to 200 ml. of solution in place of the 0.25 N hydrochloric acid which had been used previously in the other investigations. The phosphoric acid is standardized by adding 5 ml. of it to 200 ml. of conductivity water. The corrected specific conductance at 20° C. is 1925×10^{-6} reciprocal ohm. In order to have comparable analytical conditions, one liter of solution was made from each sample by diluting 40 ml. of the 25 grams in 200 ml. sirup filtrate. As in the previous studies, 4.5 grams of Domino tablet sugar were added per 100 ml. of solution before making up to the mark at 20° C. For routine work, there is a possibility that a smaller volume of solution would be sufficient, but if the cell is to be rinsed three times before each reading, it is better to have larger volumes of material.

Three conductivity determinations were made: the specific conductance of the solution, that of a solution made by taking 200 ml. of the sugar solution and adding to it 5 ml. of 0.25 N potassium hydroxide and finally the specific conductance of a solution containing 200 ml. of the sugar solution plus 5 ml. of normal orthophosphoric acid. These three values, multiplied by 10^6, will be designated as K, K_2, and K_3, respectively.

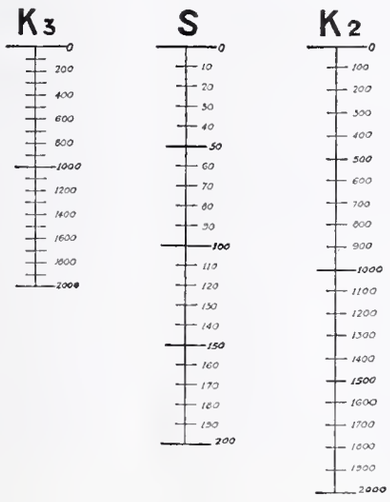
Irving Lorge, of Columbia University, made a statistical analysis of all the determinations, and by means of a technic which will be published by him elsewhere, found that the equation:

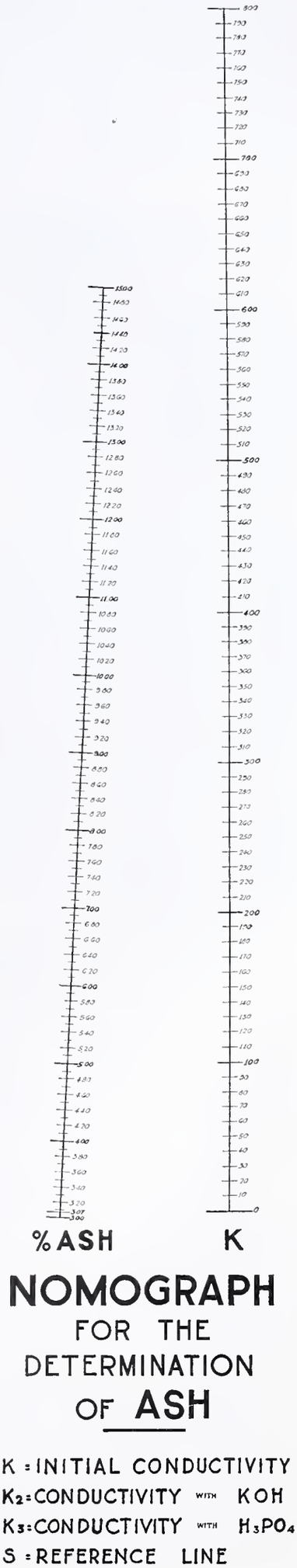
$$\text{Per cent ash} = 0.0191369\,K - 0.002249\,K_2 - 0.001210\,K_3 + 3.07 \quad (3)$$

satisfies the data.

The ash percentage may be rapidly obtained from the nomograph made by A. Bakst. A straight edge, or a thread, is laid on the values of K_3 and K_2, and the point of intersection on S is next connected with the value of K. The ash is read directly where this line intersects the per cent ash scale.

It is to be remembered that the equation applies only for solutions to which pure sucrose has been added.





In view of the results which have been obtained with the hydrochloric acid method (Formula 1), it is very likely that an equation similar to the one above might be found which would apply to solutions to which no pure sucrose has been added. The omission of sucrose would be an advantage in routine work. J. E. Mull, of this laboratory, is now making such measurements on the same samples, and the formula for calculating the ash on this basis will be published later.

Table I—Comparison between Chemical Ash and Ash Values Calculated by Formula 3

Sample	Av. Chemical Ash	Av. Calcd. Ash	Deviation of Av.	Av. Deviation	Max. Variation
Raw sugar products:					
Cuban blackstraps	9.986	9.931	−0.055	±0.146	−0.29 to +0.21
Porto Rican blackstraps	9.176	9.106	−0.070	±0.117	−0.28 to +0.17
Refinery products:					
Filtered sirups	7.393	7.552	+0.159	±0.159	+0.06 to +0.27
Unfiltered sirups	6.707	6.807	+0.100	±0.117	−0.03 to +0.19
Final sirups (X)	8.089	7.996	−0.093	±0.140	−0.30 to +0.15
Final sirups (Y)	10.274	10.281	+0.007	±0.121	−0.29 to +0.27
Final sirups, misc.	8.613	8.673	+0.060	±0.080	−0.03 to +0.19
Beet molasses (1 sample)	13.510	13.800	+0.290	±0.290	+0.29 to +0.29
Total for 133 samples	9.209	9.196	−0.013	±0.134	−0.30 to +0.29

Table I shows clearly the general applicability of the formula for various types of raw cane sugar as well as refinery products. It is of some interest to note that a beet molasses also fell into line. When it is remembered that acceptable duplicate chemical ash analyses of raw sugars may vary ±0.03 per cent on the basis of a total ash of 0.50 per cent, it is seen that the conductometric method with phosphoric acid and potassium hydroxide gives superior results for materials of low purity. In the case of the raw sugars, the tolerance amounts to 6 per cent of the total ash, while in the series under discussion the average deviation amounts to 1.4 per cent of the average ash. Furthermore, duplicate chemical analyses on low-grade products often vary enormously from laboratory to laboratory on the same sample because slight differences in the ashing technic cause great variations in the per cent ash which is reported, and so the precision with which the ash in sugar cane products can be measured by the new method is perhaps much higher than is obvious from the figures which are reported. It is true that in the final analysis the equation is based upon chemical ash determinations, but since the determinations were all made under comparable conditions, the technic would be uniform, and consequently the equation would be free from any extraneous disturbing factors. The conductometric method is rapid, and it eliminates most of the human factors which crop up in the chemical ash method.

Table II—Deviation of Average Electrical Ash for Several Products of Same Class from Average Chemical Ash of Same Samples

Sample	C-Ratio	Equation 1	Equation 2	Equation 3
Raw sugar products:				
Cuban blackstraps	+0.006	−0.098	+0.005	−0.055
Porto Rican blackstraps	+0.053	−0.023	−0.187	−0.070
All raw sugar blackstraps	+0.022	−0.078	−0.061	−0.061
Refinery products:				
Filtered sirups	−0.021	+0.011	−0.048	+0.159
Unfiltered sirups	+0.003	0.000	−0.066	+0.100
Final sirups (X)	−0.016	−0.018	−0.001	−0.093
Final sirups (Y)	−0.024	−0.026	+0.053	+0.007
Final sirups, misc.	+0.032	0.000	−0.020	+0.060
All refinery sirups	−0.015	−0.013	+0.004	+0.009

It is of interest to compare the four methods for ash determination which have been studied in this laboratory. They have been the following: the C-ratio method, the simple conductometric formula (Equation 1), the potassium hydroxide–hydrochloric acid method (Equation 2), and finally the most general method—namely, the potassium hydroxide–phosphoric acid method (Equation 3).

Table III—Average of Individual Deviation from Chemical Ash Figure for Each Kind of Product or Class of Products

Sample	C-Ratio	Equation 1	Equation 2	Equation 3
Raw sugar products:				
Cuban blackstraps	0.278	0.155	0.188	0.146
Porto Rican blackstraps	0.128	0.125	0.296	0.117
All raw sugar blackstraps	0.227	0.145	0.224	0.135
Refinery products:				
Filtered sirups	0.147	0.070	0.140	0.159
Unfiltered sirups	0.114	0.083	0.126	0.117
Final sirups (X)	0.140	0.093	0.121	0.140
Final sirups (Y)	0.240	0.158	0.112	0.121
Final sirups, misc.	0.100	0.123	0.083	0.080
All refinery sirups	0.170	0.111	0.120	0.137

As shown in Table II the potassium hydroxide–hydrochloric acid method was best for refinery products, but the potassium hydroxide–phosphoric acid method is only slightly worse whereas it shows marked improvement for the Porto Rican blackstraps as well as for the final sirups from source (Y). The C-ratio and the simple conductance methods for the Porto Rican blackstraps are even better than the new method, but the disadvantage is overcome by the consideration that the Porto Rican blackstraps now can be treated as members of the same family as the refinery sirups.

There is considerable variation among the various methods, but again it is seen that raw and refinery products are now brought quite close together. This is even clearer from Table IV.

Table IV—Maximum Individual Deviations from Chemical Ash for Each Kind of Product or Class of Products

Sample	C-Ratio	Equation 1	Equation 2	Equation 3
Raw sugar products:				
Cuban blackstraps	0.7	0.4	0.5	0.3
Porto Rican blackstraps	0.4	0.3	1.0	0.3
All raw sugar blackstraps	0.7	0.4	1.0	0.3
Refinery products:				
Filtered sirups	0.4	0.2	0.2	0.3
Unfiltered sirups	0.3	0.2	0.2	0.2
Final sirups (X)	0.4	0.3	0.3	0.3
Final sirups (Y)	0.6	0.5	0.3	0.3
Final sirups, misc.	0.2	0.2	0.2	0.2
All refinery sirups	0.6	0.5	0.3	0.3

The most striking thing about the new method is the elimination of the distinction between raw and refined products. Not only that, but in every case the method is superior to the C-ratio method where the individual idiosyncrasies of the products were taken into consideration.

Literature Cited

(1) Zerban and Sattler, *Facts about Sugar*, **21**, 1158 (1926).
(2) Zerban and Sattler, *Ibid.*, **22**, 990 (1927).
(3) Zerban and Sattler, Ind. Eng. Chem., Anal. Ed., **2**, 32 (1930).
(4) Zerban and Sattler, *Ibid.*, **2**, 322 (1930).

Mineral Production of Alaska in 1930

The Department of the Interior announces that mines in Alaska are estimated to have produced minerals to the value of $13,602,000 in 1930 as against $16,066,000 in 1929. The total value of the mineral output of Alaska since 1880 is approximately $629,000,000. The figures for 1930, which are preliminary estimates and consequently subject to revision, are taken from the Geological Survey's annual report on the mineral resources of Alaska, now in preparation. The source of this mineral wealth was approximately as follows:

Value of Mineral Output of Alaska in 1930 and 1929

	1930	1929
Gold	$ 8,394,000	$ 7,761,000
Copper	4,100,000	7,130,000
Silver	158,000	252,000
Coal	609,000	528,000
Other minerals (lead, petroleum, marble, tin, platinum, etc.)	341,000	395,000
	$13,602,000	$16,066,000

Ash and Electrical Conductivity of Refined Cane Sugars[1]

F. W. Zerban and Louis Sattler

N. Y. Sugar Trade Laboratory, 80 South St., New York, N. Y.

The percentage of ash (sulfated less 10 per cent) in refined cane sugars such as granulated and remelts, containing less than 0.3 per cent ash, can be found by dissolving 25 grams of the sugar in 100 ml. conductivity water, determining the specific conductance of the solution at 20° C., and multiplying the result, after correcting for the conductivity of the water, by the factor 530. To find the ash percentage in soft sugars, only 5 grams are used in 100 ml. solution, as in the case of raw sugars. The appropriate factor, which varies from place to place, may then be determined for each refinery, or else the general method described may be employed. The article concludes with practical recommendations for equipment and methods to be used in routine work on all types of cane products.

THIS final chapter of our investigation on the relation between ash and electrical conductivity of sugar cane products (*3* to *9*) deals with the sugars made in cane sugar refineries, and either sold or returned to process.

Work on similar products of beet sugar refineries has been reported in Europe, especially by Lundén (*1*), and on American granulated beet sugars by Nees (*2*). The last named author used a concentration of 25 grams of sugar in 100 ml., and found that for granulated beet sugars from three different states the ratio between the specific conductance $\times 10^6$ and the per cent sulfated ash (less 10 per cent) averages 231.5 if the conductivity determinations are made at 25° C. and corrected for the conductance of the water used as a solvent. The concentration of 25 grams in 100 ml. was chosen because the specific conductance passes through a maximum in the neighborhood of that point.

Granulated and Remelt Cane Sugars with Low Ash

The first group of refined cane sugars taken up by the writers comprised granulated and remelt sugars with an ash content up to 0.3 per cent. Nees' concentration of 25 grams was adopted for these low ash sugars, but the normal temperature for sugar laboratories, 20° C., has been adhered to. The same equipment was used as in all previous work, and all the solutions were filtered through a mat of filter paper and asbestos to exclude the effect of the ash contained in the insoluble portion of the sugar on the chemical ash determination. The limit of 0.3 per cent ash was arbitrarily chosen because with sugars of high ash content our standard concentration of 5 grams of sugar in 100 ml. can be used, as has been done in the case of raw sugars and also of soft sugars.

The results for 34 samples from four different refineries are given in Table I, where the sugars are arranged in the order of ascending ash content. The column headed "Chemical Ash" shows the sulfated ash, less 10 per cent, determined in the usual manner on the filtered solution of the sample. The next column shows K, the specific conductance $\times 10^6$, of the solution at 20° C., corrected for the conductance of the water. The figures in the succeeding column, headed "C-Ratio," represent the quotient of the ash percentage divided by the specific conductance itself (not $\times 10^6$). The last column gives the ash percentage calculated by multiplying the specific conductance with the average C-ratio 530, or K with 0.000530.

For the proper interpretation of these results it must be kept in mind that the different chemical ash methods themselves are all entirely empirical and do not give concordant results among each other. It will be recalled that the sulfated ash method was selected by the writers as the standard because it is affected less by details in manipulation than any of the "carbonated" ash methods. With the latter, the quantities of chlorine, sulfur, and perhaps phosphorus which are volatilized during the heating process may vary widely with slight differences in procedure. Furthermore, Lundén (*1*) has found that the sulfated ash method gives the most concordant figures when used as a basis for refinery control. Yet it is after all an empirical method and yields discrepant results in the hands of different analysts. When the ash content is very small, as in many of the samples recorded in Table I, the results even of the sulfated ash method are quite unreliable, because usually only a few milligrams or even less of ash are actually weighed, unless very large quantities of sugar are ashed, which is precluded in actual practice. In such cases the possible percentage error in the ash figure becomes enormous. The measurement of specific conductance, on the other hand, is well known to be most precise, and for this reason alone the electrical ash method, although admittedly empirical, is, nevertheless, to be preferred over the other empirical ash methods. In addition to this, it is much more rapid, and much more easily executed.

Table I—Ash and Conductivity of Unwashed and Washed Granulated and Remelt Sugars, with Ash up to 0.3 Per Cent

Sample	Chemical Ash	Specific Conductivity $\times 10^6$ (K)	C-Ratio	$K \times$ Av. C-Ratio
	%			
1	0.0059	11.7	504	0.0062
2	0.0077	16.1	478	0.0085
3	0.0088	19.6	449	0.0101
4	0.0095	22.6	420	0.0120
5	0.0110	16.5	671	0.0087
6	0.0112	16.5	679	0.0087
7	0.0128	20.6	621	0.0109
8	0.0158	31.8	497	0.0169
9	0.0292	59.1	492	0.0313
10	0.033	63.4	524	0.034
11	0.035	63.1	554	0.033
12	0.039	77.5	503	0.041
13	0.052	111.8	441	0.059
14	0.071	124.4	571	0.066
15	0.073	134.3	544	0.071
16	0.079	147.9	534	0.078
17	0.083	178.4	465	0.094
18	0.084	156.9	536	0.083
19	0.096	189.5	507	0.100
20	0.110	247.5	445	0.131
21	0.114	204.5	558	0.108
22	0.118	181.3	651	0.096
23	0.124	206.4	602	0.109
24	0.130	233.9	556	0.124
25	0.134	253.1	530	0.134
26	0.146	293.3	498	0.155
27	0.167	334.5	500	0.177
28	0.169	319.9	528	0.170
29	0.172	357.4	481	0.189
30	0.175	314.0	557	0.166
31	0.177	346.9	510	0.184
32	0.225	431.7	521	0.229
33	0.226	367.2	599	0.195
34	0.269	460.0	585	0.244
35	0.295	566.2	521	0.300
		Av.	530	

[1] Received September 18, 1930. Presented before the Division of Sugar Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

One difficulty arises in the case of specially purified sucrose, and some refined sugars of the very highest grade. With sugars of this type the specific conductance of the solution may be less than the specific conductance of the water, owing to the depressing effect of sucrose on the conductivity of electrolytes. In cases like this, specially purified water might be used, but even then the difficult question of correction would remain. With such sugars the ash content can be found only approximately, yet with greater precision than by the chemical method.

It is interesting to inquire how the C-ratio of 530 found for refined cane sugars compares with the C-ratio of granulated beet sugars. At 25° C., the temperature used by Nees, the value 530 would be reduced to 470. Nees' divisor, 231.5 at 25° C., is equal to a C-ratio of 432. This confirms the statement of Nees that the ratio between ash and conductivity for cane sugars is probably different from that for beet sugars, because the latter contain a large proportion of highly ionizable alkali salts. This would involve a lower C-ratio for granulated beet sugars, in agreement with the facts.

With this class of sugars it is obviously unnecessary to resort to the more complicated conductometric procedures of ash determination, developed by the writers for raw sugars and for sirups and molasses.

Soft Sugars

The chemical ash in the samples of soft sugars received by the writers from three different refineries ranged from 0.18 to 2.31 per cent. The conductivity determinations were therefore run on solutions containing 5 grams of total sugar in every 100 ml. of solution, as in the case of raw sugars. Within the ash range up to 1 per cent, 5 grams of the soft sugar were used, and above 1 per cent, 2.5 grams of soft sugar plus 2.5 grams of sucrose; in the latter case the result of the conductivity determination was multiplied by 2. Parallel determinations were made in the presence of acid, 5 ml. of 0.25 N hydrochloric acid being added to 200 ml. of the 5-gram-per-100-ml. sugar solution, and measuring the specific conductance again, exactly as in the previous work. The results of the measurements are shown in Table II. Columns 1 to 5 are the same as in Table I. The average C-ratio was found to be 1580 which is lower than the value found previously for any group of refinery products, but this fact has little significance because it has been shown before that the C-ratio may vary within extremely wide limits. Column 6 gives the individual deviations of the electrical ash (in column 5) from the chemical ash. The values for K_1, which is the specific conductance $\times 10^6$ of the acidified solution, are found in column 7. In column 8 are shown the figures for the ash calculated by the simple conductometric expression developed previously ($0.913\ K + 193.5 - 0.1\ K_1$), multiplied by the factor 0.001695. This factor agrees closely with the average factor obtained for refinery sirups (*8*).

The individual errors by the C-ratio method exceed 0.03 per cent in seven cases, amounting to 0.04 in two, 0.05 in one, 0.08 in two, and 0.12 in one. The total deviations for this method are −0.52 and +0.51, or 1.03 in all. The conductometric formula results in only two deviations of 0.04 per cent and two of 0.05 per cent; the total deviations are −0.30 and +0.41, or 0.71 altogether. The simple conductometric formula method is evidently more reliable than the C-ratio method, and still better results could probably be obtained by the general conductometric formula based on three conductivity determinations (*9*), one on the solution itself, a second after addition of N orthophosphoric acid, and a third after addition of 0.25 N potassium hydroxide solution. But it is believed that this would have no practical advantage, and in the control of a single refinery even the C-ratio method will probably prove quite satisfactory for most purposes.

Table II—Ash and Conductivity of Soft Sugars

Sample	Chemical Ash	K	C-Ratio	$K \times$ Av. C-Ratio	Error	K_1	Ash Calcd. by Formula	Error
	%				%		%	%
1[a]	1.30	829.6	1567	1.31	+0.01	1824	1.32	+0.02
2[a]	1.43	900.2	1589	1.42	−0.01	1776	1.45	+0.02
3[a]	1.53	983.4	1556	1.55	+0.02	1755	1.58	+0.05
4[a]	1.84	1149.4	1601	1.82	−0.02	1717	1.85	+0.01
5[a]	2.31	1385.8	1667	2.19	−0.12	1573	2.27	−0.04
6	0.43	280.5	1497	0.44	+0.01	2143	0.40	−0.03
7	0.46	308.3	1492	0.49	+0.03	2184	0.44	−0.02
8	0.60	399.4	1502	0.63	+0.03	2098	0.59	−0.01
9	0.79	506.2	1561	0.80	+0.01	2045	0.77	−0.02
10	0.89	563.4	1580	0.89	0.00	1931	0.87	−0.02
11[a]	1.07	695.6	1538	1.10	+0.03	1945	1.07	0.00
12[a]	1.23	807.8	1523	1.28	+0.05	1970	1.24	+0.01
13[a]	1.26	813.0	1550	1.28	+0.02	1889	1.27	+0.01
14[a]	1.50	963.8	1556	1.52	+0.02	1821	1.53	+0.03
15[a]	1.49	940.2	1585	1.49	0.00	1767	1.51	+0.02
16[a]	1.63	1013.8	1608	1.60	−0.03	1756	1.63	0.00
17	0.27	178.2	1515	0.28	+0.01	2077	0.25	−0.02
18[a]	1.47	892.0	1648	1.41	−0.06	1528	1.52	+0.05
19	0.42	276.6	1518	0.44	+0.02	2020	0.41	−0.01
20	0.21	136.4	1540	0.22	+0.01	2067	0.19	−0.02
21[a]	1.84	1110.6	1657	1.76	−0.08	1474	1.87	+0.03
22	0.80	509.4	1570	0.80	0.00	1770	0.82	+0.02
23[a]	1.52	942.4	1613	1.49	−0.03	1633	1.56	+0.04
24	0.63	413.9	1522	0.65	+0.02	1946	0.64	+0.01
25[a]	1.26	777.2	1621	1.23	−0.03	1770	1.26	0.00
26	0.83	541.9	1532	0.86	+0.03	1898	0.84	+0.01
27[a]	1.72	1036.4	1660	1.64	−0.08	1613	1.71	−0.01
28	0.28	199.1	1406	0.32	+0.04	2113	0.28	0.00
29	0.19	126.8	1498	0.20	+0.01	2135	0.17	−0.02
30	0.45	299.4	1503	0.47	+0.02	2054	0.44	−0.01
31	0.22	167.7	1312	0.26	+0.04	2153	0.22	0.00
32	0.59	375.1	1573	0.59	0.00	2044	0.56	−0.03
33	0.18	132.7	1356	0.21	+0.03	2150	0.17	−0.01
34	0.87	533.2	1632	0.84	−0.03	1795	0.85	−0.02
35	0.48	309.3	1552	0.49	+0.01	1942	0.48	0.00
36	0.60	387.6	1548	0.61	+0.01	1934	0.60	0.00
37	0.75	490.3	1550	0.77	+0.02	1855	0.77	+0.02
38	0.89	565.8	1573	0.89	0.00	1748	0.91	+0.02
39[a]	1.31	832.2	1574	1.31	0.00	1811	1.33	+0.02
40[a]	1.29	824.6	1564	1.30	+0.01	1825	1.31	+0.02
41[a]	1.31	812.2	1613	1.28	−0.03	1815	1.30	−0.01

[a] The conductance determinations on these samples were made at a concentration of 2.5 grams sample plus 2.5 grams sucrose, and the results were multiplied by 2.

High Ash Remelt Sugars

The samples collected by the writers included six remelt sugars with an ash content within and also above the soft sugar range. The conductivity determinations were therefore made at the concentration adopted for soft sugars—that is, on 5 grams sample in every 100 ml. up to an ash content of about 1 per cent; at an ash content between 1 and 3 per cent, 2.5 grams sample plus 2.5 grams sucrose were taken, and when the ash exceeded 3 per cent, 0.5 gram sample plus 4.5 grams sucrose were used. The results are given in Table III.

Table III—High Ash Remelt Sugars

Sample	Chemical Ash	K	C-Ratio	$K \times 1580$	Error	K_1	Ash Calcd. by Formula	Error
	%				%		%	%
1	0.39	245.1	1591	0.39	0.00	1936	0.38	−0.01
2	0.66	375.3	1759	0.59	−0.07	1723	0.62	−0.04
3	1.35	814.2	1658	1.29	−0.06	1709	1.34	−0.01
4	2.05	1193.2	1718	1.88	−0.17	1443	2.01	−0.04
5	3.25	1985.0	1637	3.14	−0.11	1891	3.15	−0.10
6	4.63	2761.0	1677	4.36	−0.27	1734	4.61	−0.02

The discrepancies found by the C-ratio method, with the average C-ratio of 1580 for soft sugars, are rather large, but, as has been explained above, without significance. The results calculated by the simple conductometric formula, with the soft sugar factor 1695, are very much better, considering that an error of 0.10 on 3.25 per cent ash is really only about 3 per cent of the total. Just as with the soft sugars, the general conductometric formula mentioned above would probably reduce the errors, but in practice it is unnecessary to go to such refinements.

Summary of Recommendations for Routine Electrical Ash Determinations in Sugar Cane Products

EQUIPMENT—For routine conductivity measurements it is advisable to use a self-contained instrument with as little outside wiring as possible, to prevent current leaks and other inconveniences. If it is operated by a battery this should also be enclosed in the instrument case. With this type a telephone receiver is necessary as a null indicator. In a noisy factory laboratory the telephone is practically useless, and if alternating line current is available or can be provided, it is better to use an instrument to be connected to the a. c. line with a galvanometer as null indicator. The only other outside connection should be with the conductivity cell. The instrument should be calibrated in terms of specific conductance at 20° C.; this necessitates a compensator for variations in the cell constant. For cane products it is not advisable to have the scale calibrated directly in ash percentage, on account of the variations in the C-ratio, but an additional blank scale might be provided which could be calibrated by the individual worker for the C-ratio most frequently used. The instrument should also be provided with a compensating device for variations in temperature. Since the temperature coefficient itself varies to some extent as has been shown by the writers, especially when conductivity determinations are made also in the presence of acid and alkali, it is safest to keep the temperature of the solution as close as possible to the standard of 20° C. This is most readily accomplished by the use of the Lange type of cell provided with a water jacket, as employed by the writers. This cell has the further advantage for routine work that the solution which has been tested can be run out rapidly and the next solution be filled in without delay. Dipping cells may also be used if preferred, but they are not as convenient as the Lange type of cell.

METHOD—For the control work of individual factories it is desirable and quite possible to use the ordinary C-ratio procedure, with only one conductivity determination, based on actual comparisons of chemical ash and specific conductance of the various products. These should include not only the materials studied by the writers, but should be extended to the several types of juices.

When samples are received from many different sources, such as in regulatory and similar work, the choice of the proper method will depend on the type of product analyzed. For granulated and other refined sugars of low ash content, the simple C-ratio method outlined in this paper is sufficiently accurate. For raw cane sugars and soft sugars the simple conductometric formula with two conductivity determinations should be used, the factor being 0.001757 for raw sugars (*7*), and 0.001695 for soft sugars. The same method, with the factor 0.01757, will also suffice for sirups and molasses known to have been produced without char treatment (*8*), but otherwise it is safest to resort to the general conductometric formula based on three conductivity determinations, one on the solution itself, one with the addition of phosphoric acid, and one with the addition of potassium hydroxide (*4*).

Acknowledgment

The writers are indebted to various sugar refining companies in the New York district for the samples used in this investigation.

Literature Cited

(1) Lundén, *Z. Ver. deut. Zuckerind.*, **75**, 763 (1925).
(2) Nees, IND. ENG. CHEM., **19**, 225 (1927).
(3) Sattler and Zerban, *Facts about Sugar*, **23**, 686, 713 (1928).
(4) Sattler and Zerban, IND. ENG. CHEM., Anal. Ed., **3**, 38 (1931).
(5) Zerban and Mull, *Facts about Sugar*, **21**, 278 (1926).
(6) Zerban and Sattler, *Ibid.*, **21**, 1158 (1926).
(7) Zerban and Sattler, *Ibid.*, **22**, 990 (1927).
(8) Zerban and Sattler, IND. ENG. CHEM., Anal Ed., **2**, 32 (1930).
(9) Zerban and Sattler, *Ibid.*, **2**, 322 (1930).

The Plastometer[1,2]

A New Instrument for Measuring Plastic Properties of Coal

Joseph D. Davis

U. S. BUREAU OF MINES, 4800 FORBES ST., PITTSBURGH, PA.

BETWEEN certain limiting temperatures, depending on its rank and to some extent on its origin, a coking coal assumes a semi-fused or plastic state. Destructive distillation of the coal substance and of those constituents which fuse, begins as soon as or before fusion sets in and is greatly accelerated by rising temperature; the mass may assume a more or less plastic state before solidifying as coke. As the temperature rises to the limit of the plastic range (or state), most of the volatile matter is driven off and the mass sets into coke. Plasticity develops, however, only when a favorable heating rate, such as that prevailing in industrial coking practice, is chosen. Audibert (*2*) has shown, for example, that it is possible to choose a heating rate so slow that the fusible matter is decomposed before it has actually fused. In such a case the coal does not become plastic and coke is not formed. On the other hand, heating may be so rapid that, although fusion does take place, decomposition is accelerated to such an extent that plasticity cannot be measured and a frothy coke results. The instrument to be described was designed in connection with the Bureau of Mines Survey of the Gas- and Coke-Making Properties of American Coals, for heating rates within the range of those prevailing in industrial practice under these conditions. Coke is invariably produced, provided that the coal is suitable for coke-making.

[1] Received September 19, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Printed by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Previous Methods for Studying Plastic State of Coal

The method devised by Foxwell (*3*) and modified by Layng and Hathorne (*4*), and that of Agde and von Lyncker (*1*) will serve as examples of experimental methods previously used for study of the plastic state of coal.

Layng and Hathorne carbonize a standard column of sized coal at a suitable rate in an electric tube furnace while passing nitrogen through it. Sufficient nitrogen for the test is confined in a bottle connected to the tube containing the coal. This is caused to flow by water displacement at constant head, so that resistance to its passage develops when the coal fuses. A manometer connected to the nitrogen

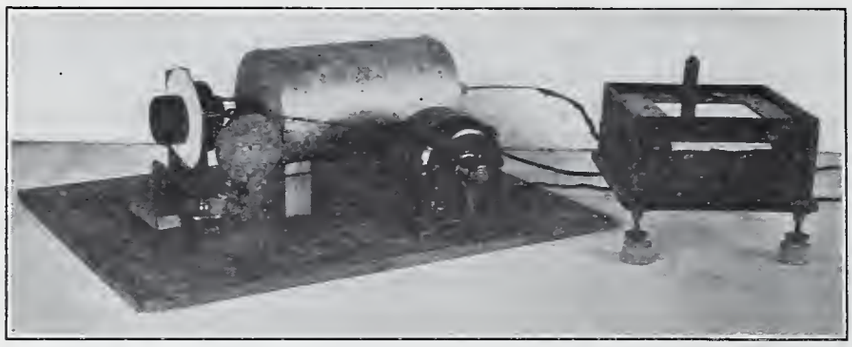


Figure 1—The Plastometer

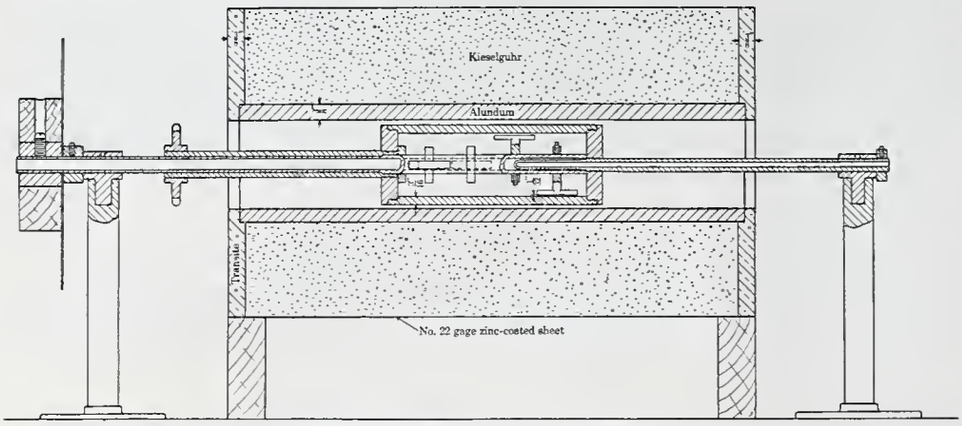


Figure 2—Diagram of Plastometer

bottle serves to indicate the amount of resistance and the rate at which it develops. This is plotted against the temperature (or time) and defines the plastic range of the coal.

Agde and von Lyncker carbonize a small sample of coal packed in a vertical tube furnace at a constant heating rate. A weighed needle, which is free to move vertically, rests on the coal. When the coal fuses the needle begins to sink and the rate of sinking is noted on a vertical scale provided for the purpose. The more plastic the coal the more rapid is the rate of sinking. When the charge sets into coke the needle comes to rest.

Although the Layng-Hathorne method with most coals serves to define approximately the limits of the plastic range, it does not give a direct measure of the plasticity of the charge within this range. The Agde-von Lyncker method, on the other hand, gives a figure which corresponds with the ease with which the charge yields to a needle. It is in effect a penetrometer, and the result obtained is not necessarily a measure of plasticity. In addition, it defines the limits of the plastic range with more or less precision.

In the hands of the writer this method proved difficult to carry out, yielding results difficult of close reproduction.

Without discussing the relative merits of these methods it is perhaps sufficient to observe that, when properly carried out, both will yield specific information of considerable value to one studying the coking process. Of course great care must be employed in interpretation of such results.

The specific information sought by the plastometer is the plasticity of the charge within the plastic range, together with close definition of the temperature limits.

Description of Plastometer

Figure 1 is a photograph of the plastometer and Figure 2 shows a vertical section through the instrument. The plastometer consists of a steel retort 5 inches (127 mm.) in length by $1^7/_8$ inches (22 mm.) in diameter, mounted on a tubular axle through the center of a 2-inch (51-mm.) tube furnace 12 inches (305 mm.) in length, and arranged for rotation at constant speed by a $^1/_4$-horsepower motor through a reduction gear and chain drive. The retort, whose wall is $^3/_{16}$ inch (4.8 mm.) in thickness, is provided with screw caps. A tubular shaft is passed through the gear-driven axle into the retort. Five rabble arms are fixed to the end of this shaft within the retort. These arms clear the retort wall by $^1/_{32}$ inch (0.4 mm.). The protruding end of the shaft is fitted with a circular brass disc whose rim carries a scale similar to that of a torsion viscometer head. A pulley is also fixed to the end of the shaft and a chain is attached to its face. The other end of the chain is fixed to a spiral tension spring; as long as the rabble arms within the retort encounter no resistance in the rotating retort, the shaft does not turn and the spring is under no tension.

Method of Making Test

Eight grams of the 20- to 40-mesh coal sample[3] to be tested are charged into the retort and the heads are screwed in place, a thick paste of graphite and oil being used to prevent the threads from "freezing" on subsequent heating. The charged retort is now placed in the furnace, the drive chain is attached, and a thermocouple is inserted in the hollow shaft. The temperature is given continuously by a recording milli-

[3] It is recognized that the selection of a size fraction of coal is not representative of the entire coal, and it is hoped to modify the apparatus so that a strictly representative sample in which the fine coal is not rejected may be used.

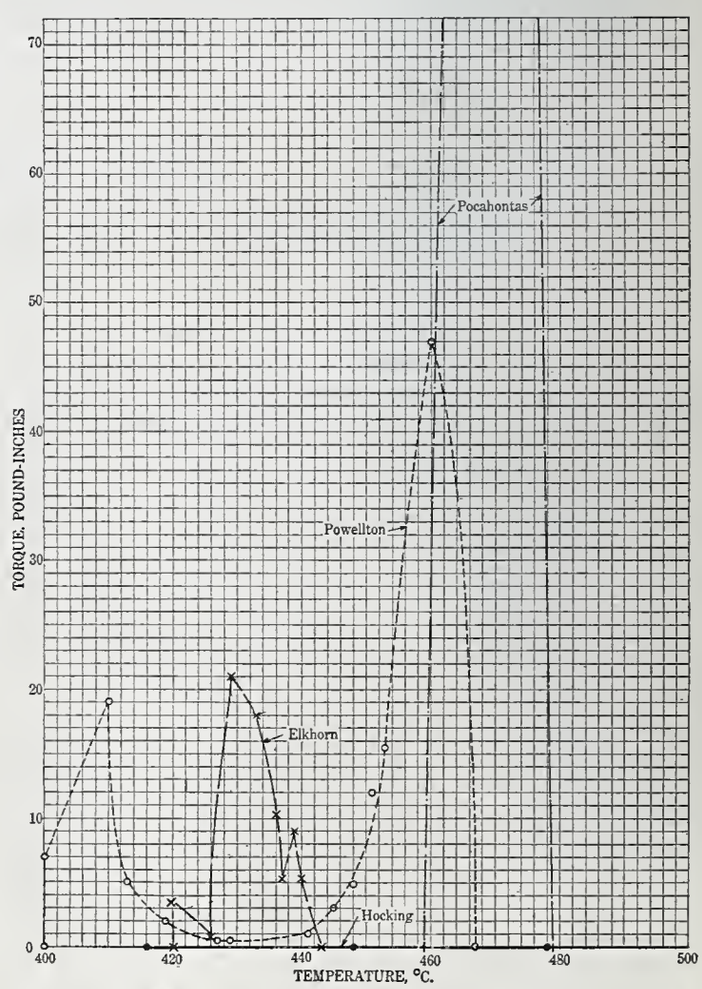


Figure 3—Resistance Developed in Heating Coal in Plastometer

voltmeter. The motor is now started and the furnace is rapidly heated (7° C. per minute) to approximately 375° C., below which point no tension of the coil spring develops. From 375° C. through the plastic range (480° to 500° C.) the heating rate is maintained constant (± 0.2°) at 3.4° C. per minute. A note of the scale reading is made at 1-minute intervals during the plastic range and at the end of the experiment the readings, reduced to pound-inches of torque, are plotted against the temperature. Tension develops at 400° to 460° C. depending on the coal, and drops sharply at temperatures ranging from 450° to 480° C. The plastic range is defined by these limiting temperatures for each coal.

Behavior of Different Kinds of Coal under Test

By the manner of development of tension on the plastometer head several kinds of coking coals have been distinguished:

(1) Coals that fuse at a low temperature, have a wide plastic range, and become very plastic at intermediate temperatures. These coals fuse together well and should produce well-fused coke—i. e., the Powellton coal of Figure 3.

(2) Gas coals containing splint that have a short plastic range and exhibit little or no plasticity, as the Elkhorn coal.

(3) Semi-bituminous coals having a high fusing temperature, very little plasticity, and a short plastic range which gives an exceedingly high plastic tension, as shown by the Pocahontas coal of Figure 3.

(4) High oxygen, weakly coking coals of which the limiting temperatures of the plastic range are just distinguishable by the plastometer. Hocking coal represents this type.

Practical Value of Plastometer

Only a few coals have been tested by this method and no broad generalization can be made as to indication of coke quality. However, with coals so far tested it may be observed that: (1) Class 1 coals produce a fine-grained coke which does not fracture badly when exposed to high coking temperatures; (2) class 2 coals have large cells and when coked without admixed low-volatile coals give a more fractured high-temperature coke than class 1 or class 3 coals; (3) class 3 coals produce strong fine-grained coke but one which does not shrink appreciably after setting and which offers resistance to pushing from ovens.

Literature Cited

(1) Agde, G., and von Lyncker, L. V., *Brennstoff-Chem.*, **10**, 86–7 (1929).
(2) Audibert, E., *Rev. ind. minérale*, **1926**, 115–36.
(3) Foxwell, G. E., *J. Soc. Chem. Ind.*, **40**, 193–201T, 220T (1921).
(4) Layng, T. E., and Hathorne, W. S., Ind. Eng. Chem., **17**, 165 (1925). See also Layng, T. E., and Coffman, A. W., *Ibid.*, **19**, 924 (1927), and **20**, 165 (1928).

Determination of Alkalinity of Reclaimed Rubber[1]

Henry F. Palmer and George W. Miller

Xylos Rubber Company, Akron, Ohio

A new method is given for determining the relative alkalinity of reclaimed rubber. The extraction of the alkaline material is based on a digestion of the sample in a mixture of ethanol, benzene, and water. The method is compared with the previous method described by the authors in 1928. The experimental figures given show that the new method gives results which are dependable, and approximately four times as accurate as the previous method. The higher degree of accuracy is due to the elimination of much of the personal error, the extraction of a larger percentage of alkaline material, and a more accurate titration end point.

THE purpose of this paper is to present a method for determining the relative alkalinity of reclaimed rubber which, in the authors' opinion, has certain advantages over other methods in use at present.

In general other methods current for determining alkalinity consist of a digestion in water of various sizes of samples for times varying from 3 to 48 hours. In the discussion of an article by Shepard, Palmer, and Miller (*2*) in 1928, the relative control method then in use by the authors was described. This method has recently been referred to by Stafford (*3*) in an article on the testing of reclaimed rubber. Briefly this method consists in digesting a 25-gram sample in water for 3 hours, after which the sample is squeezed and thoroughly washed during squeezing. The sample is further digested, and the liquor titrated with normal acid using methyl red as the indicator. A disadvantage of this method is that it involves a personal factor in the squeezing of the sample after digestion. Another disadvantage of the method and other unpublished methods known to the authors, is that a relatively small quantity of the total alkali is extracted which naturally means that errors in the method will magnify the differences in alkalinity. Further, the solution to be titrated is often brown enough in color so that the end point of the usual indicators is masked. The method developed and described below overcomes these difficulties since a relatively higher percentage of alkaline material is removed and a more efficient titration method is applied.

Method of Titration

Inasmuch as the color of the solution often causes the end point of usual indicators such as methyl red to be very indistinct, an application has been made of the iodine-starch end point. The procedure after the sample is prepared for titration is as follows:

To the solution 0.1 *N* HCl is added from a buret until the solution is distinctly acid. This point may be most definitely determined by using litmus paper. Approximately 5 cc. each of 3 per cent KIO_3 solution and of 1 *N* KI solution are then added. The mixture is allowed to stand 3 minutes and the same volume of 0.1 *N* $Na_2S_2O_3$ as 0.1 *N* HCl is added. The mixture is allowed to stand for 15 minutes after which 5 cc. of fresh starch solution are added. Titration is then made with 0.1 *N* iodine solution until the appearance of the usual iodine-starch blue color. This color may of course be black due to the brown color of the solution.

The particular advantage of this method of titration is that the end point can always be distinguished and even the darkest solutions can be diluted so that the end point is visible. In cases of reclaim of low alkalinity the solutions are less deeply colored and the end point may often be de-

[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

termined by the use of methyl red instead of the iodine-starch combination.

It should be mentioned that before arriving at the above method an effort was made to use the two following methods:

(1) Use of $K_2Al_2(SO_4)_4.24H_2O$: Since $K_2Al_2(SO_4)_4$ hydrolyzes in water to H_2SO_4 and $Al(OH)_3$, the H_2SO_4 reacts to neutralize the alkali and the $Al(OH)_3$ carries down a considerable amount of colloidal matter in the solution, but not enough to render the solution sufficiently clear to discern methyl red indicator.

(2) Use of $FeCl_3$ and $K_4Fe(CN)_6.3H_2O$: When $FeCl_3$ hydrolyzes in water to form HCl and $Fe(OH)_3$, the HCl will neutralize the alkaline material. Any soluble ferric salt gives with $K_4Fe(CN)_6$ a very deep blue color. In using this method $FeCl_3$ was added until all the alkali was neutralized, the blue color being formed by the excess $FeCl_3$ with $K_4Fe(CN)_6$. The color was masked considerably, however, by the presence of the $Fe(OH)_3$. The addition of HCl to diminish the amount of $FeCl_3$ necessary was not effective since the indicator was not sensitive to such a small amount of $FeCl_3$.

Extraction of Alkaline Material

Since other methods in vogue have extracted a relatively small amount of the total alkaline material, an effort was made to evolve a method which would give a higher percentage of the total alkali present. This has been achieved by the use of the following procedure:

The sample of reclaim is sheeted to a thickness of 0.127 mm. (0.005 inch) plus or minus 0.0254 mm. (0.001 inch) in thickness. A 5-gram sample is torn in pieces about 25 mm. (1 inch) in diameter and placed in a liter Erlenmeyer flask to which have been added 60 cc. of benzene, 40 cc. of ethanol (denatured with 0.5 per cent benzene),[2] and 100 cc. of distilled water. These reagents must, of course, be neutral. A reflux condenser is attached to the flask and digestion is made for 2 hours on a hot plate which is at 110° C. After the digestion 500 cc. of distilled water are added and the heating continued for $1^1/_2$ hours without the reflux condenser attached. At the end of this time the benzene and the larger percentage of the ethanol will be completely distilled off. If benzene is still present at the end of this time, the heating, with a periodic shaking, should be continued until all benzene is removed. The total heating time will not exceed $1^3/_4$ hours. The solution is then decanted leaving the rubber sample in the flask. Seventy-five cubic centimeters of boiling distilled water are added and the flask whirled rapidly to wash the sample. This water is added to the original liquid and two more washings are made as above after which the solution is allowed to cool preparatory to titration.

In developing this method of extraction the following observations have been made on factors which affect the results:

Thickness of Sample—The same sample of reclaim was refined once and twice at the thicknesses of 0.0762 and 0.1778 mm. (0.003 and 0.007 inch) with the results shown in Table I. The results reported in all tables are in terms of NaOH. These results show that the thickness between these limits may be tolerated and that the second refining did not affect the amount of alkaline material extracted. An attempt was made to prepare the sample by cutting it into very small pieces but the results in Table II show that this is not a suitable method of preparation.

Effect of Benzene, Ethanol, and Water—Various proportions of benzene, ethanol, and water were tried. The first tests were run with 100 cc. benzene, 100 cc. water, and 20 cc. ethanol. The benzene functions to swell and break up the rubber and the ethanol acts as a carrier. With these proportions it was found that the emulsion formed made it difficult to boil off the benzene without much bumping, foaming, and spattering. The benzene was decreased and the ethanol increased to the proportions named in the method with the result that the above mentioned difficulties disappeared.

The effect of these reagents in different proportions is given in Table III. It will be noted that increasing the volume of water gives no higher results. The ethanol is necessary as a carrier and the benzol as a swelling agent. Tests on another sample of reclaim A show 0.242 per cent alkalinity when the regular volume of reagents was doubled, against 0.238 per cent for the prescribed volume.

[2] 2B Formula, U. S. Industrial Alcohol Co.

Table I—Effect of Refining (Reclaim A)

Thickness of Sample		Number of Refinings	Alkalinity		
			Test 1	Test 2	Av.
Mm.	*Inch*		%	%	%
0.0762	0.003	1	0.312	0.300	0.306
0.0762	0.003	2	0.283	0.293	0.288
0.1778	0.007	1	0.272	0.279	0.276
0.1778	0.007	2	0.280	0.292	0.286

Table II—Comparison of Methods of Preparing Sample (Reclaim G)

Method of Preparation	Alkalinity	
	Test 1	Test 2
	%	%
Sheeted on refiner mill	0.420	0.412
Cut into $^1/_8$-inch (3-mm.) cubes	0.365	0.216

Table III—Effect of Digesting Reagents

Reclaim	Test	Alkalinity			
		Benzene, cc. 60 Ethanol, cc. 40 Water, cc. 100	60 40 200	100 .. 100	.. 100 100
		%	%	%	%
A	1	0.304	0.318	0.127	0.179
	2	0.305	0.304	0.122	0.212
D	1	0.505	0.462	0.248	0.453
	2	0.507	0.462	0.248	0.406

Effect of Time of Digestion—A sample of reclaim A was digested for 2 and 3 hours with the extraction of 0.164 per cent and 0.165 per cent alkali, respectively. Observation showed that times less than 2 hours are insufficient to break up the sample thoroughly.

Amount of Water Added after Digestion—Whether the water added after digestion is cold or hot did not affect the alkalinity value. The water caused the finely divided and benzene-swollen sample to form a semi-solid mass so that the benzene could be boiled off without any danger of loss of sample or liquor due to spattering. Five hundred cubic centimeters gave higher alkalinity results than lower volumes and were used as a practical upper limit convenient to handle.

Number of Washings—After decanting the liquor from the sample it was convenient to wash the sample in the flask. In washing with 75-cc. portions of hot water, it was found that the alkaline material became constant after the first washing. The alkalinity determination on the various washings will be found in Table IV.

Table IV—Effect of Washing

	Alkalinity			
	Reclaim B		Reclaim C	
	Test 1	Test 2	Test 1	Test 2
	%	%	%	%
Determined from decanted liquor only	0.094	0.106	0.470	0.466
Washings with 75 cc. hot water:				
(1)	0.004	0.008	0.010	0.010
(2)	0.004	0.004	0.004	0.004
(3)	0.004	0.004	0.004	0.004

Error Caused by Retention of Liquor by Sample—It is obvious that the sample retains some alkaline liquor, and since in the new method the sample is not squeezed, this is a source of error. In Table V is shown the approximate amount of liquor retained and the percentage error introduced by its retention.

Table V—Error Due to Liquor Retained by Sample

	Reclaim B	Reclaim C
	Cc.	*Cc.*
Decanted liquor plus washings	825	825
Liquor retained by sample	25	23
Total liquor	850	848
	%	%
Alkalinity as determined on available liquor	0.114	0.486
Corrected alkalinity based on total liquor	0.118	0.503
Error due to liquor held by sample	3.4	3.2

Effect of Iron and Antimony Compounds on Results—The fact that trivalent antimony may be titrated with iodine led to the following experiment to determine whether iron or antimony would affect the results as obtained by an iodometric titration.

Two per cent of crimson antimony (Sb_2S_3) were added to a whole tire scrap (reclaim A) and refined on the laboratory mill. To another sample of scrap, 5 per cent of red oxide (Fe_2O_3) were added and the reclaim finished as before. These were tested against a control reclaim made from the same sample of well-blended scrap. The figures given in Table VI show that trivalent antimony in the reclaim affects the titration with iodine while red oxide has no effect.

Table VI—Effect of Iron and Antimony Compounds Added to Reclaim A

	Alkalinity			
	Test 1	Test 2	Av.	Variation
	%	%	%	%
Control	0.350	0.354	0.352	....
5% Red oxide (Fe_2O_3)	0.351	0.354	0.353	+0.001
2% Crimson antimony (Sb_2S_3)	0.299	0.301	0.300	−0.052

Table VII—Comparison of Old and New Methods on Several Samples of Different Reclaims

Reclaim	Sample	Operator	Old Method			New Method		
			Test 1	Test 2	Variation	Test 1	Test 2	Variation
A	1	Z	0.047	0.050	0.003	0.272	0.261	0.011
	2	Z	0.028	0.040	0.012	0.225	0.225	...
	3	Z	0.103	0.099	0.004	0.242	0.251	0.009
B	1	Z	0.019	0.020	0.001	0.100	0.097	0.003
	2	Z	0.022	0.014	0.008	0.116	0.116	...
	3	Z	0.044	0.037	0.007	0.167	0.167	...
	4	W	0.034	0.038	0.004	0.100	0.110	0.010
	5	W	0.056	0.055	0.001	0.136	0.139	0.003
	6	W	0.044	0.049	0.005	0.141	0.140	0.001
	7	W	0.041	0.046	0.005	0.111	0.122	0.011
	8	W	0.060	0.056	0.004	0.157	0.163	0.006
D	1	X	0.429	0.397	0.032	0.507	0.505	0.002
E	1	Z	0.180	0.164	0.016	0.374	0.382	0.008
	2	Z	0.216	0.217	0.001	0.386	0.386	...
F	1	X	0.013	0.012	0.001	0.064	0.055	0.009
H	1	X	1.68	1.94	0.260	1.91	1.83	0.08
I	1	X	0.819	0.585	0.234	0.96	1.05	0.09

Table VIII—Reproducibility of Results by Different Operators

Reclaim	Operator	Alkalinity		
		Test 1	Test 2	Variation
NEW METHOD AND SAME SAMPLE				
		%	%	%
B	X	0.123	0.126	0.003
B	Y	0.130	0.126	0.004
C	X	0.487	0.484	0.014
	Y	0.488	0.474	0.014
	Z	0.488	0.488	...
G	X	0.406	0.400	0.006
	Z	0.420	0.412	0.008
OLD METHOD AND SAME SAMPLE TITRATED WITH METHYL RED				
		Test 1	Test 2	Test 3
		%	%	%
A	X	0.083	0.099	0.062
A	Z	0.110	0.158	0.163

The experimental work given below was carried out on reclaims which will be designated as follows:

A—a regular production whole tire reclaim
B—a specially washed whole tire reclaim
C—an experimental whole tire reclaim
D—an experimental whole tire reclaim
E—a carcass reclaim
F—a digester tube reclaim
G—a whole tire reclaim processed in another factory
H and I—tube reclaims processed in another factory

Table IX—Continuous Total Extractions

Time of Extraction	Alkalinity	
	Reclaim A	Reclaim B
	%	%
First 24 hours	0.375	0.089
Days		
6	0.716	0.345
11	0.837	0.508
16	0.899	0.608
21	0.953	0.684
26	0.999	0.750
31	1.018	0.783
36	1.030	0.814
41	1.038	0.837
46	1.045	0.860
51	1.048	0.865
55	1.048	0.865
Percentage extracted:		
Old method	0.150[a]	0.034[a]
New method	0.307[b]	0.126[a]
Percentage of total:		
Old method	14.31	3.93
New method	29.29	14.57

[a] Average of 2 tests.
[b] Average of 4 tests.

The tests given in Table VII show a comparison of the method of extraction previously used (*2*), except that the redigestion for 2 hours was not used, with the benzene-ethanol method described above. All titrations were made with the iodine-starch end point. This table shows the variation which occurs with the old method in comparison with the new method. It will be noted that the new method extracts two to five times as much alkaline material and consequently the percentage error in the new method is much

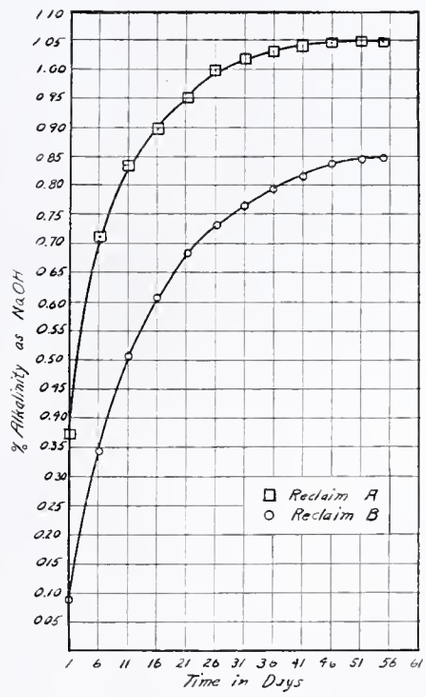


Figure 1—Complete Extractions of Reclaims A and B

less than in the old method, assuming equivalent actual error in the test. However, examination of the figures in Table VII will show a less actual error in the new method, and consequently a much higher accuracy. The average error shown by these figures is 15.62 per cent for the old method and 4.06 per cent for the new method. The results show also that the new method lines up different samples of the same reclaim better than the old method, which shows considerable variation between different samples.

Tests run on the same sample of reclaim by different operators show that this method is not subject to the personal error which is caused primarily by the squeezing. The old method, however, cannot be depended upon to give reproducible results by the same or different operators as Table VIII shows.

In order to compare the amount of alkaline material actually present with that extracted by the old and new method, a complete extraction was made on reclaims A and B. It was necessary to run this for 55 days until the percentage of alkaline material removed corresponded to the blank. Twenty-five-gram samples were digested in 800 cc. of boiling water continuously. At first the water was changed every 24 hours, while near the end of the experiment it was changed every 48 hours. Kilbourne and Miller (*1*) required about 60 days for determination of total alkalinity. Samples of the same reclaims were also run by the old and new method. The results, given in Table IX, show that the old method extracts 14.31 per cent and the new method 29.29 per cent in reclaim A, and in the case of reclaim B, 3.93 per cent of the total was extracted by the old method and 14.57 per cent by the new. While it is possible to achieve as high results as are given by the benzene-ethanol method by continued extraction in water for at least 24 hours and upwards to 48 hours, this length of time is hardly practicable. The benzene-ethanol method may be completed in approximately 5 hours.

Acknowledgment

The authors are indebted to O. C. Moyer for his helpful suggestions and analytical work.

Literature Cited

(1) Kilbourne and Miller, Ind. Eng. Chem., **22**, 69 (1930).
(2) Shepard, Palmer, and Miller, *Ibid.*, **20**, 143 (1928).
(3) Stafford, *Trans. Inst. Rubber Ind.*, **5**, 340 (1930).

Purification of Perchloric Acid by Vacuum Distillation[1]

G. Frederick Smith and O. E. Goehler

Department of Chemistry, University of Illinois, Urbana, Ill.

Special designs of stills for the purification of perchloric acid by vacuum distillation are described including besides conventional designs a cold target type. Special features involved in the vacuum distillation of perchloric acid are shown to govern the design of the still to be used in its purification.

The variation in the acid concentration of both distillate and residue with change in pressure over the range 1 to 7 mm. is given.

The separation of perchloric acid from various amounts of sulfuric and phosphoric acids by vacuum distillation is subjected to a careful quantitative examination, and the conditions under which complete separations result are described. The time rate of distillation of various designs of stills is determined and the rate of distillation shown to be directly proportional to the degree of superheating employed.

The preparation of pure perchloric acid by all methods of manufacture requires that it be purified by distillation. Distillation of perchloric acid at atmospheric pressure results in too great a loss through the formation of chlorine, oxygen, and water. The vacuum distillation of perchloric acid is complicated by the pronounced tendency the distilling liquid shows to superheating. This phenomenon of superheating, together with consideration of the pressure applied during distillation, is closely related to the rate of distillation. The object of the present paper is the study of the various factors influencing the design of vacuum distillation equipment for the purification of perchloric acid and its use in the separation by distillation from sulfuric and phosphoric acids.

Special Properties Associated with Vacuum Distillation of Perchloric Acid

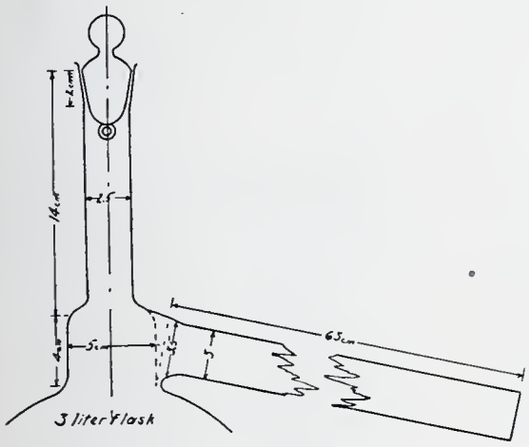
The vacuum distillation of concentrated perchloric acid of approximately the constant boiling composition (72.4 per cent at 760 mm.) up to the composition of the dihydrate (73.60 per cent) shows the following distinctive features: The distilling acid can be superheated to the extent of 30° to 60° C. depending upon the pressure and the rate of application of heat. A thermometer placed in the liquid being distilled and another placed at varying heights in the vapors over the liquid will show wide differences in temperature depending upon the amount of superheating and the difference in level of the thermometer bulbs within and above the distilling liquid. The acid, therefore, is not in simple equilibrium with the vapors formed. The complex nature of the mixture of different forms of perchloric acid in this vapor phase is the subject of a subsequent paper. By regulating the pressure between the limits 0.0 to 18.0 mm., the temperature of the distilling liquid can be varied between 50° and 120° C. The distillate under these conditions collects at the rate of 0.5 to 10 cc. per minute. No ebullition accompanies such distillations. Even with agitation of the strongly superheated distilling acid, no ebullition results.

If the perchloric acid being distilled under reduced pressure contains dissolved gases some preliminary ebullition results. There are two methods of eliminating these dissolved gases: Chill the strong (71 to 72 per cent) acid before distillation to a temperature of −5° to −10° C. or lower. This method has the additional advantage that solids in solution, such as sodium, potassium, or other perchlorates, are also removed. Or first concentrate the perchloric acid to be distilled at atmospheric pressure until a temperature of approximately 200° C. is attained and the acid concentration has reached 71.5 to 72 per cent using the same still for the concentration as that to be employed in the vacuum purification. The temperature of the concentrated acid is then allowed to fall to from 80° to 90° C. and the distillation continued at reduced pressure.

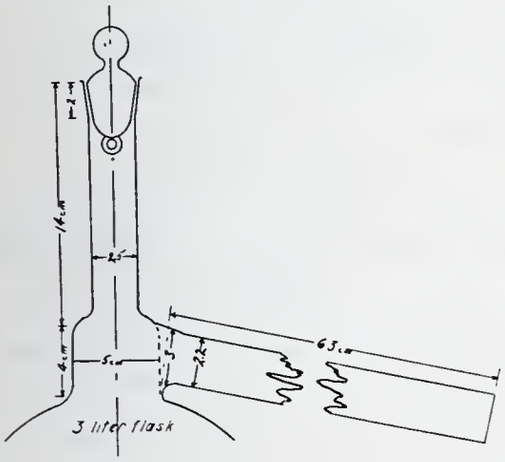
[1] Received August 23, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Control of Factors Leading to Rapid Distillation by Changes in Still Design

Several factors govern the design of a still for the purification of perchloric acid. The main ones are: First, the efficient condensation of the distilling vapors. This problem is made the more important by the fact that the vapors are at a temperature much higher than minimum distillation temperature because of the superheated condition of the distilling liquid. Second, the use of a target type of condenser can be predicted as most efficient in both condensation



AA



BB

Figure 1—Stillheads of Conventional Design

of the vapors emitted and in avoiding return flow of condensate. Third, the control of the degree of superheating by regulation of the pressure. This last factor is influenced in turn by the first two.

Dimensions Applied to Stills of Conventional Design

Figure 1 shows two stillheads with dimensions included. The important dimensions are those of the inside diameter of the condenser tube and its length. As shown, the point of contact between the condensing side arm and the neck of the flask is placed as close to the balloon of the flask as indicated. This is possible because the liquid is distilling without ebullition and is advisable to prevent return flow of condensed acid vapors. A 5-liter flask has been used successfully in connection with this design of still. This design does not provide for recovery of the condensed acid forming on the inside of the neck above the side arm. The length of the condenser arm was found to be suited to the use of ordinary tap water for cooling.

As a result of the tests upon stills *AA* and *BB* given in Table I, it is observed that the latter gave both the best yield of finished product per unit of time and resulted in the greatest degree of superheating. A maximum application of heat which just failed to produce ebullition was employed.

Modification of Cold Target Design of Still

According to the explanation of the mechanism accounting for the phenomenon of superheating to be given in a later paper, the molecules of gaseous perchloric acid are projected through a probable film of oxonium perchlorate (OH_3ClO_4) upon the surface of the distilling liquid. In taking advantage of this phenomena and for the additional advantage of making the distillation apparatus more compact the cold target type of still illustrated in Figures 2 and 3 were designed and tested. These are of two types, those of *A* and *B*, Figure 2, which provide for the application of the pump connection at the end of a vertical condensing column and a refluxing of the condensed acid vapors to be drained out at the lower horizontal outlet shown. Neither type *A* nor *B* was found to be suited by comparison with the conventional form of still shown in Figure 1. This type of still has a further disadvantage that if operated at pressures greater than 7 mm. there is some probability that anhydrous perchloric acid may be formed in some quantity and fail to be condensed before passage through the pumping system. The stillheads *C* and *D*, Figure 2, and the design shown in Figure 3 were found more efficient in condensing the distilling vapors and in addition are more compact. The drawings of Figure 2 do not show the condenser chamber water-cooling jackets in place. The performance of these (Figure 2) stills, with the exception of type *A*, is shown in Table I.

The most satisfactory still design of all those studied is shown in Figure 3. This type differs from those of Figure 2 in that the double ring seal at the top of the distilling flask is eliminated and the length of the tubular from the top of the distilling flask into the condensing chamber is changed. It was observed in the cold target type of condenser that practically all of the vapors condensed at the upper end of the cooled target which is in accordance with the fundamental principles underlying the construction of such a still. The cooling surface is thus materially diminished. The ground stopper used to charge the still and support the thermometer (an Anschütz of range 50° to 105° C.) also provides for the use of a little concentrated perchloric acid to seal the stopper against leaks. The receiving flask is attached using a rubber stopper and the connection made to the vacuum pump using rubber pressure tubing. This form of still provided for the greatest degree of superheating and the best time rate of distillation, as shown in Table I. It is the most easily charged and recharged of those designs shown and is by far the most compact. It is more expensive than the conventional type of Figure 1, which is practically its only disadvantage. All the subsequent tests of the present paper were made using this type of distillation equipment.

Table I—Rate of Distillation and Working Temperature of Various Types of Perchloric Acid Vacuum Stills at 1 to 2 mm. Pressure

Type	Distillation Rate	Temperature Maximum	Temperature Average	Distillation Rate 50° C.
	Kg. per hour	*° C.*	*° C.*	*Kg. per hour*
AA	1.05	77	75	0.20
BB	1.14	89	85	0.18
B	0.90	86	84	0.10
C	1.04	90	88	0.10
D	0.93	91	85	0.10
Fig. 3	1.19	94	93	0.08

An examination of the data of Table I shows the superiority of the distillation apparatus designed according to Figure 3. The maximum rate of distillation is seen to accompany the greatest degree of superheating and the highest

average temperature of distillation. The strength of the acid distilled in these tests was 71 to 72 per cent.

Further Considerations in Purification of Perchloric Acid

Crude perchloric acid made from technical grades of ammonium perchlorate after concentration to from 70 to 72 per cent strength at atmospheric pressure will have, after cooling and gravity separation of the solid perchlorate impurities (potassium, sodium and ferric perchlorates, and dehydrated silica), variable amounts of soluble impurities to be removed by vacuum distillation. The degree of dehydration of silicic acid and the extent to which soluble impurities are removed will depend upon the temperature applied during the concentration at atmospheric pressure and the temperature to which the acid is chilled prior to the separation of solid impurities.

Crude ammonium perchlorate is made by a large number of technical modifications of essentially the same process, and the degree of purity depends upon the particular process employed and upon the question of its purification by recrystallization. Varieties of crude ammonium perchlorate containing appreciable amounts of potassium perchlorate are particularly objectionable, but varieties having as high as 5 to 6 per cent of sodium perchlorate are profitably employed in the manufacture of perchloric acid. The natural tendency is to fail to concentrate the crude acid to a temperature of approximately 200° C. at atmospheric pressure in the preparation of 72 per cent acid for vacuum distillation. This is because appreciable decomposition of the hot acid results, a great portion of which decomposition takes place at 190° to 200° C. This decomposition can be almost completely eliminated by using large enough vessels in the concentration at ordinary pressures. Twenty-liter, round-bottom, Pyrex flasks serve well. Starting with such a flask of dilute (20 to 30 per cent) perchloric acid, at the point of concentration to 72 per cent acid the flask is approximately one-third full. Under these conditions the known tendency (*1*) of the concentrating acid to form lower hydrates which decompose, is offset by their reaction with the water vapor being expelled which counteracts their decomposition into chlorine and oxides of chlorine. Concentration to 72 per cent crude perchloric acid has the additional advantage that soluble impurities become less soluble to be removed later by chilling. In the distillation of even the crudest of perchloric acid, the process can be carried out until two-thirds of the starting material is distilled, and with more pure forms until 90 per cent of the starting product has distilled. This process of distillation which includes no ebullition makes it particularly suited to the freeing of perchloric acid from soluble solids because of the absence of spray from the distilling liquid.

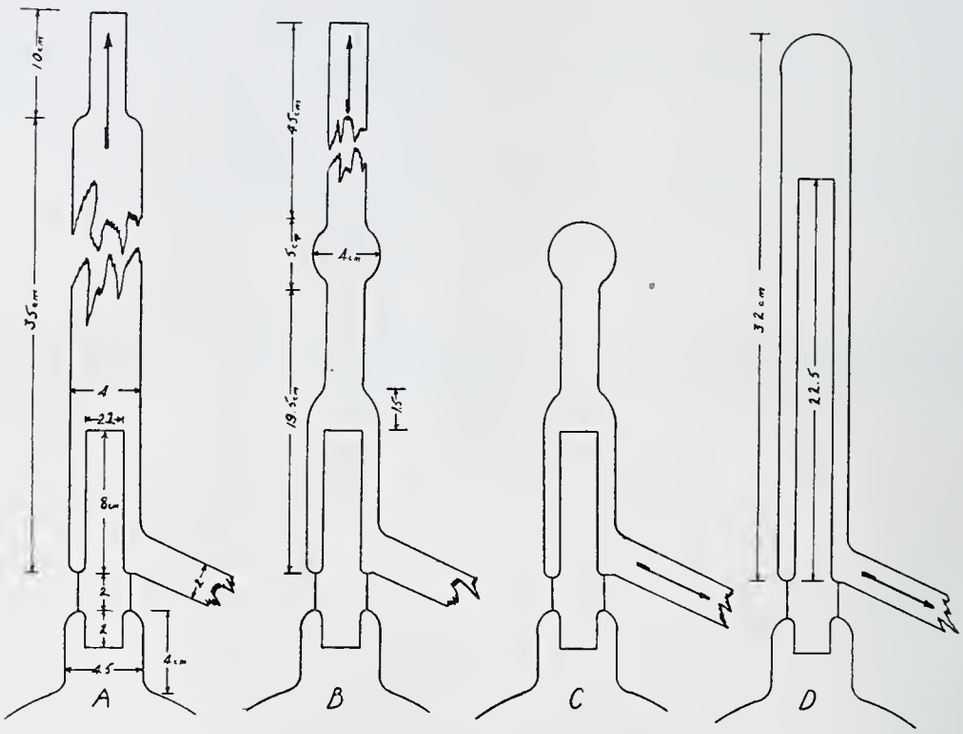


Figure 2—Types of Cold Target Stills

Variation in Acid Strength as Governed by Pressure of Distillation

The distillation of 73.60 per cent perchloric acid was carried out using the still design of Figure 3 at various pressures from 0.5 to 7.0 mm. The variation in the composition of the distillate and undistilled residue in the distilling flask was then examined by the determination of the density of the products obtained. The data obtained were of importance because of their bearing upon a process for the preparation of perchloric acid dihydrate by vacuum distillation. The method of determining the density of the various acids thus obtained will be given in a subsequent paper. The results of these determinations are given in Table II.

Table II—Variation in Acid Concentration Resulting from Distillation of 73.60 Per Cent Perchloric Acid at Pressures between 0.5 and 7 mm.

Pressure	Distillate Density 25°/4° C.	Residue Density 25°/4° C.	Difference Density	Acid in Residue-Distillate
Mm.				%
0.5–1	1.71600	1.71621	0.00021	+0.15
2.0–2.5	1.71545	1.71520	0.00025	+0.18
4.0–4.5	1.71383	1.71416	0.00033	+0.23
6.5–7	1.71211	1.71190	0.00021	−0.15

An examination of this table shows that the maximum difference obtained in acid composition between distillate and residue between the range 0.5 to 7 mm. is 0.30 per cent. Thus by plotting the values obtained from the density of the acid of the distillate at various pressures of distillation as a function of the acid composition, it is observed that the pressure producing acid of the exact dihydrate composition is 5.7 mm. The plot of the data is shown in Figure 4. The

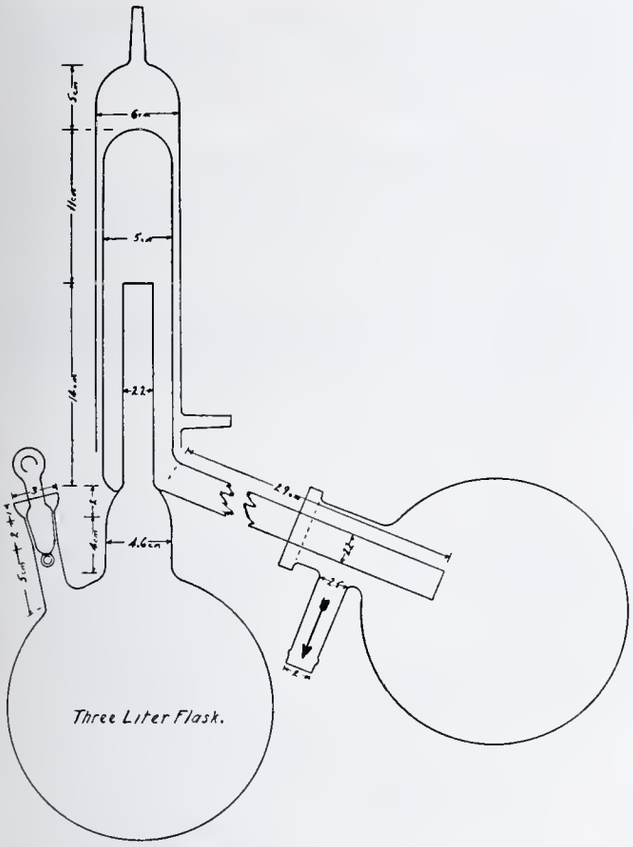


Figure 3—Design for Cold Target Still

density of the exact dihydrate was taken from unpublished data as 1.71282 at 25°/4° C.

Separation of Perchloric Acid from Sulfuric and Phosphoric Acids

The cheapest method of manufacture in the preparation of perchloric acid consists in the oxidation of ammonium perchlorate (*1*). By this process any ammonium sulfate or phosphate impurity in the raw materials would result in a contamination of perchloric acid produced, which would require the purification of the same by a distillation process capable of separating perchloric acid from sulfuric and phosphoric acids. The study was therefore made by this separation using the vacuum still of Figure 3, at varying pressures and with varying amounts of contaminating sulfuric and phosphoric acids.

The process in the case of both sulfuric and phosphoric acid was as follows: 71 to 72 per cent perchloric acid was adulterated with known quantities of sulfuric and phosphoric acids in separate determinations starting with 2 per cent by weight of the particular acid as impurity. The distillation was then carried out until a given portion of distillate was collected at a given pressure of distillation and the distillate set aside for further examination. The residue in the still, assuming the amount of contaminating acid carried over in the first operation was small, has a new ratio of contaminating acid which can be tested for complete separation by a further distillation. The second distillate is then set aside for analysis and the process continued. The extent of the contamination of the acid being distilled may then be taken as the mean of the starting and finishing concentrations.

The extent of the contamination of the distillate of perchloric acid by the sulfuric or phosphoric acid was determined in each case by its second distillation under the same conditions with an analysis of the total residue in the still for the contamination involved. The accuracy of this process depends upon the practically complete separation of the contaminant in one operation.

It would be predicted from a general knowledge of the variation in vapor pressure with the temperature that the separation of perchloric acid from both sulfuric acid and phosphoric acid would be more complete the lower the pressure of distillation. It would also be predicted that the sulfuric acid contamination would be the most difficult to remove. In the case of the mixed solutions of sulfuric and phosphoric acids with perchloric acid studied, the contamination was purposely made far more extensive than would ever be the case in the use of any serviceable stock of ammonium perchlorate for the manufacture of perchloric acid. The data resulting from the study of this purification are given in Table III.

Table III—Separation of Perchloric Acid from Sulfuric and Phosphoric Acids at Several Temperatures and Pressures

Perchloric acid used, 71–72%; volumes distilled, 500 to 3000 grams, per cent acid distilled, 50%

Contaminating Acid		Temperature	Pressure
At start	In distillate		
%	*Gram*	° *C.*	*Mm.*
Sulfuric acid			
0.2	0.0000	65–80	1
2–4	0.0039	105	10
4–5.73	0.0042	105	10
2–4.1	0.0013	75–85	1
4.1–6.2	0.0024	75–85	1
6.2–10.4	0.009	75–85	1
Phosphoric acid			
3.5–12.8	None	75–85	1
12.8–19.9	None	75–85	1
19.9–36	Trace	75–85	1

The following conclusions can be drawn from the experiments listed in Table III.

For the separation of perchloric acid from sulfuric acid, if the contamination of the distillate is to be restricted to 0.001 per cent, the original impurity of sulfuric acid must not exceed 4 per cent and the pressure and temperature of the distillation must be as low as possible. The possible contamination is slowly increased by allowing the pressure to increase together with the temperature. The amount of

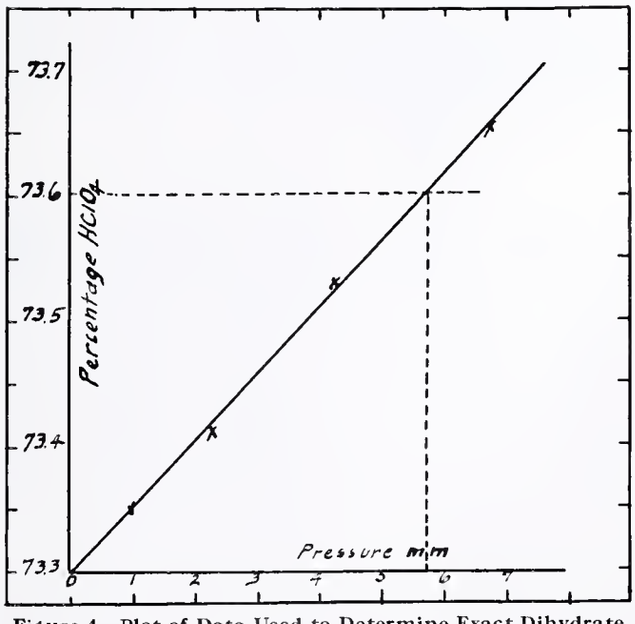


Figure 4—Plot of Data Used to Determine Exact Dihydrate Composition of Perchloric Acid

sulfuric acid is not more than 0.004 per cent up to a concentration of 6 per cent of sulfuric acid in the product purified even under the most unfavorable conditions of temperature and pressure. The amount of sulfate in crude ammonium perchlorate is never great enough to require that the perchloric acid made from it be twice distilled *in vacuo* in order to completely free it from sulfuric acid.

The separation of perchloric acid from phosphoric acid is not a problem even up to a contamination of 36 per cent if the temperature and pressure of the distillation is low, and probably the separation is equally good under the most unfavorable conditions. The data obtained in connection with the separation of perchloric acid from phosphoric acid prove that no contamination of the distillate resulted from spray produced by ebullition or otherwise mechanically. This fact proves that the process is particularly adapted to the separation of perchloric acid from solid impurities by distillation.

Literature Cited

(1) Willard, *J. Am. Chem. Soc.*, 34, 1480 (1912).

Perchloric Acid as a New Standard in Acidimetry[1]

G. Frederick Smith and W. W. Koch

Department of Chemistry, University of Illinois, Urbana, Ill.

A still design to be used in the preparation of standard 73.60 per cent perchloric acid by vacuum distillation is described and a study made showing the variation in product within the pressures 2 to 7 mm.

An indirect method of analysis has been employed combining the use of constant boiling hydrochloric acid and a precision type of Foulk chain hydrometer in the analysis of 73.60 per cent perchloric acid obtained by this process.

Explanation is made of the effect upon and control of variables known to be related to the process described.

THE object of this paper is the description of a process for the preparation by vacuum distillation of perchloric acid to be used as a standard in acidimetry. The product obtained corresponds most closely to the dihydrate ($HClO_4 \cdot 2H_2O$, theory 73.603 per cent $HClO_4$). Within the limits of the pressure range used in this process, 2 to 7 mm. of mercury, the product obtained agrees with the composition of the true dihydrate as well as the analysis of the product can be determined, 73.60 ± 0.03 per cent, or an accuracy of one part in approximately 2500. It will be shown that the conditions of preparation are conveniently attained and easily duplicated.

Briefly the process is as follows: Perchloric acid of 72 per cent strength is distilled in a properly designed still at 2 to 7 mm. pressure until half the product has been fractionated. The distillation is interrupted and the distillate discarded. The residue is then distilled under the same conditions to obtain the standard product.

Distillation Apparatus

The apparatus, shown in Figure 1, consists of a modified Claisen flask, *A*, 500 cc., fitted with a ground glass stopper with hook for supporting an Anschütz thermometer 50° to 100° range. The side arm of the flask is sealed at the top and the condenser jacketed portion provided with the ground glass terminal shown, to which the 500-cc. receiving flask, *C*, is attached. The side arm of the flask *A* should provide an opening leading to the condenser tube approximately 12 mm. wide instead of 20 to 25 mm. as is ordinarily the case with the unmodified flask. Condenser *B* should provide 200 to 225 mm. of cooling surface length and the inner tube should be 10 mm. inside diameter. Flask *C* connects through its side arm to a good rotary oil pump. Between flask *C* and the oil pump is a differential mercury gage of the closed tube type reading pressures over a range of 0 to 20 mm. and should be accurate to ±0.5 mm. Between flask *C* and the oil pump is placed a soda-lime tube 25 to 35 mm. in diameter by 200 mm. long provided at each end with a 13 to 15 mm. adaptor. An air release inlet tube should be placed between the flask *C* and the soda-lime tube. Rubber tubing is used to make connections on the pump side of flask *C*. The ground glass union in the neck of flask *C* may be replaced by a rubber stopper. Condenser *B* employs a moderate stream of cold tap water.

Distillation Operation

The unusual features of the distillation operation in the case of perchloric acid have been fully described in another paper (*3*) and reference to this paper must be made for a correct understanding of this operation. The vacuum distillation of perchloric acid is not a hazardous operation. All pure perchloric acid of commerce is prepared by vacuum distillation. It is well to conduct the operation out of possible contact with wood or other inflammable material as fire may result in case of breakage. The distillation of perchloric acid under atmospheric pressure is accompanied by some decomposition to form chlorine, oxygen, and water. Such decomposition does not occur in the process described.

Table I—Boiling Point and Density of Various Perchloric Acid Solutions

$HClO_4$	B. P. 760 mm.	Density 15°/4° C.	Density 25°/4° C.	$HClO_4$ Distillate
% by wt.	*° C.*			*% by wt.*
56.65	148.0	1.49	1.48	...
61.2	162.3	1.55	1.54	0.9
65.2	181.2	1.61	1.60	6.06
70.06	198.7	1.67	1.66	40.11
71.0	200.8	1.69	1.67	...
72.4	203.0	1.71	1.69	72.4

Selection of Perchloric Acid Used as Starting Material

Perchloric acid is usually purchased in the form of a 60 per cent solution. A solution of 72 per cent acid is more satisfactory and can now be obtained from the better supply houses. It may be made conveniently following the Willard (*8*) method of the oxidation of pure ammonium perchlorate with nitric and hydrochloric acid. Pure acid is preferred but relatively impure or "commercial" acid may be purchased and purified by distillation under reduced pressure. The distillation of constant boiling perchloric acid (the 72.4 per cent acid of Table I) may be carried out at atmospheric pressure but the loss by decomposition is appreciable. Acid less concentrated than 72 per cent may be converted to the constant boiling strength by boiling at 760 mm. until the temperature reaches 203° C. Decomposition begins at 60 per cent acidity and increases in amount as the reaction temperature increases. Two methods serve for its rough analysis, the determination of its density or its boiling point. Values for use in this connection are given in Table I. These

[1] Received August 23, 1930.

values were found by reference to the work of van Wyk and van Emster (*9,1*).

Preparation of Materials

Perchloric Acid—Prepared by the method of Willard (*8*). For other method see Goodwin and Walker (*4*) (anodic oxidation of hydrochloric acid).

Barium Hydroxide—Prepared approximately 0.1 *N* from pure barium hydroxide dissolved in conductivity water with filtration into resistance glass bottles containing air free from carbon dioxide. It was preserved out of contact with carbon dioxide at all times and was standardized before use and again after most of it had been used up. Precisely concordant results were obtained for both standardizations.

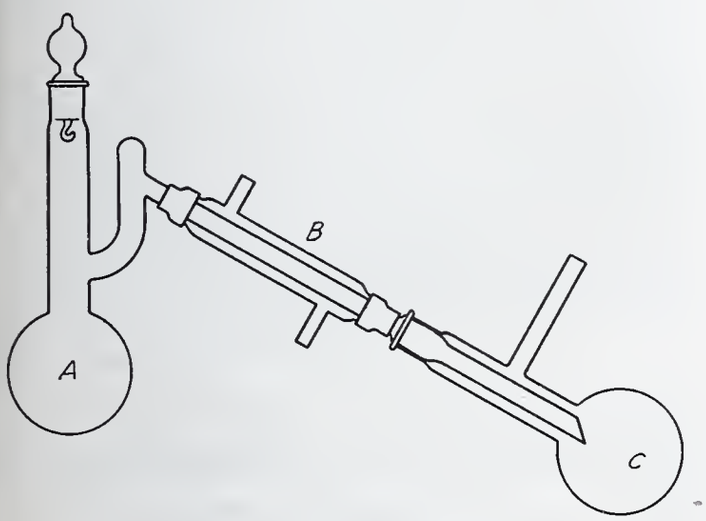


Figure 1—Distilling Apparatus

Standard Acid—Constant boiling hydrochloric acid was prepared following in every detail the directions of Foulk and Hollingsworth (*2*).

Indicator—The sodium salt of dibromothymolsulfonphthalein (bromothymol blue) was prepared as described by Lubs and Clark (*6*). The color change from yellow at a pH of 6.0 to blue at pH of 7.6 with green at the transition point, serves both in natural and in artificial light. Correction was made for the small amount of standard solution necessary for the end point color change.

Water—Conductivity water was used throughout.

Method of Analysis

Sampling—Both the constant boiling hydrochloric acid and the samples of perchloric acid were weighed in small 2-cc. glass bulbs having finely drawn capillary openings (miniature Dumas vapor density bulbs). These were filled by bending the capillary openings into a V shape, placing the open end within the sample to be taken contained in a small test tube, and warming the bulb to displace the air within by the acid of the sample. The sampling ampules were then cooled to room temperature and the capillary opening sealed by fusion with a fine blast flame. The difference between the weight of the sample tube and contents and the empty sampling tube, corrected for the weight of the fine capillary tube sealed off, gave the weight of the contents. The weight of the sample was not corrected for the weight of air over the sample which was somewhat different before and after sealing because of temperature effects. This correction was in all cases negligible for the reason that the sample tubes were nearly full in each case.

Weighing—All weighings were made using a Troemner balance accurate to ±0.02 mg. The weights used were calibrated by the Bureau of Standards and buoyancy corrections were applied.

Preparation and Titration of Samples—The filled sampling ampules, together with the capillary tube from the same, were added to a titration beaker. The sampling bulb and the capillary tube were broken and crushed under 100 to 150 cc. of water and a measured portion of the indicator solution added. The acid was then titrated with the standard barium hydroxide solution using weight burets (*7*). The weight of acid taken corresponded to from 100 to 200 grams of titrating solution. Both the standardization of the barium hydroxide solution against constant boiling hydrochloric acid and the titration of the unknown perchloric acid samples were carried out in exactly the same way.

Yield of Perchloric Acid as Function of Strength of Starting Material

In order to obtain data concerning the rate of concentration resulting from the vacuum distillation of various strengths of starting material, a fractional distillation of three different starting concentrations was made. The data are recorded in Table II.

Table II—Fractional Distillation of Perchloric Acid
1–5 to 7.5 mm. pressure; 2000 cc. still

Fraction	Weight *Grams*	Fraction Distilled *% by vol.*	$HClO_4$ %	Av. $HClO_4$ %
		70 per cent acid		
1	190	9.0	51.03 51.07	51.05
2	290	12.0	66.72 66.75	66.74
3	300	11.0	72.49 72.52	72.51
4	230	9.0	73.03 73.08	73.06
5	220	8.6	73.02 72.98	73.00
6	225	8.8	73.31 73.35	73.33
7	113	4.4	73.09 73.09	73.09
Residue	932	36.5	73.65 73.65	73.65
		71 per cent acid		
1	190	7.8	61.09 61.13	61.11
2	230	9.1	67.15 67.16	67.16
3	240	9.3	71.31 71.30	71.31
4	260	9.9	72.90 72.86	72.88
5	250	9.5	73.45 73.45	73.45
6	260	9.8	73.52 73.54	73.53
7	99	3.5	72.64 72.63	72.63
Residue	1070	40.5	73.55 73.55	73.55
		72 per cent acid		
1	191	7.9	60.02 60.03	60.02
2	253	9.8	69.24 69.21	69.23
3	254	9.5	72.00 72.00	72.00
4	254	9.5	73.08 73.05	73.06
5	294	10.9	73.02 73.00	73.01
Residue	1417	52.5	73.59 73.54	73.57

As shown in Table II the yield of acid corresponding most closely to the dihydrate ($HClO_4 \cdot 2H_2O$) from 70, 71, and 72 per cent perchloric acid as starting material is 36.5, 40.5, and 52.5 per cent by volume, respectively. It is therefore advantageous to start with the 72 per cent acid in order to arrive at the best yield of the finished product. Concentration takes place rapidly in all cases up to the 73 per cent range after approximately 35 per cent by volume has been distilled. Less rapid concentration results after 73 per cent acid concentration is reached, but the yield from all three starting strengths is excellent for this type of preparation.

Factors Influencing Selection of 2 to 7 mm. as Pressure Range of Distillation Yielding Standard 73.60 Per Cent Perchloric Acid

The complex nature of the various possible dissociations of perchloric acid to form the different known hydrates during vacuum distillation over the pressure range 0 to 18 mm. has been fully discussed in another paper (*3*). From this work, which should be consulted for a proper understanding of the reactions involved, it is apparent that above 7 mm. pressure the distillate starting with 73.6 per cent acid strength contains the following hydrates of perchloric acid: $HClO_4.3H_2O$, $HClO_4.2H_2O$, and $HClO_4$ (anhydrous). Depending upon the ratio of the various hydrates formed, which in turn depends upon the pressure of distillation, it would be predicted that a distillate of varying composition would be obtained. The distillate obtained at 7 mm. pressure and below most nearly corresponds to 73.60 per cent perchloric acid (*3*).

Below 7 mm. pressure any variation in the acid concentration as a result of the formation of other hydrates than the dihydrate ($HClO_4.2H_2O$) is corrected for in the use of the still described in Figure 1. The side arm of the Claisen flask *A* provides a reflux chamber in which the other two forms $HClO_4.3H_2O$ and $HClO_4$ (anhydrous) are caused to combine and reflux into the distillation chamber. Variations in pressure below 7 mm. result in the formation of a distillate of such uniform composition, therefore, using the apparatus described, that the process conforms practically to the requirements leading to a method for the preparation of a new standard for acidimetry.

Determination of Lower Limit of Pressure Permissible in Process Employed

If the upper limit of pressure as indicated (*3*) is 7 mm. for all practical purposes, there remained the determination of the lower limit below which the distillation could not be carried out without appreciably affecting the acid concentration of the distillate. This was determined using the apparatus of Figure 1 with the 73.60 per cent perchloric acid and gradually decreasing pressures starting with 7 mm. The lower limit found by the analysis of the distillate at various pressures below 7 mm. was 2 mm. This is not a serious handicap since without the use of special equipment a pressure less than 2 mm. is hard to attain with the apparatus described. Furthermore the magnitude of the possible error is small as shown in the following manner:

The 73.6 per cent perchloric acid was distilled in an apparatus similar to that of Figure 1 except that all ground joints were eliminated by glass seals and a mercury vapor pump and liquid air trap used to increase the vacuum produced by the oil pump. Distillations were carried out using a pressure range of 0.02 to 0.1 mm. as determined using a McLeod gage.

Three hundred and twenty-three grams of acid were distilled and 150 grams of distillate obtained. A second portion of 360 grams of acid was distilled and 130 grams of distillate obtained. The two residues were then combined and 200 grams from these distilled. A distillate of 115 grams was thus obtained and the residue of 85 grams analyzed. It was found to be 73.8 per cent perchloric acid. The analyses of the preliminary residues showed that most of the concentration that has resulted took place in the early stages. The analyses of the distillates showed them to be correspondingly weak in acidity, 73.27 per cent. The temperature during these distillations varied between 60° and 70° C. There is, therefore, little danger of error due to distilling at too low pressure.

Preparation and Analysis of Constant Strength Perchloric Acid for Use as New Standard of Acidimetry

To test the application of the apparatus described and the pressure range determined, a series of acid samples were prepared in the apparatus described using approximately 72 per cent perchloric acid as starting material and various pressures between 2.2 and 7.0 mm. Most of these preparations were carried out at 3.5 to 5.0 mm. pressure since this range represents the mean between the two extreme pressures permissible; 300 to 400 cc. of 72 per cent perchloric acid were distilled and the samples taken from the second fraction after the original material had been half distilled.

The samples of standard perchloric acid were analyzed by an indirect method depending upon the determination of their relative density. Two reference samples, one greater and one lower in density, were then carefully analyzed as previously described. Assuming a linear relationship to exist between the density and percentage composition of samples intermediate in density between the two reference solutions, the percentage composition of the sample being analyzed was determined graphically. That such a linear relationship exists was determined by van Emster (*1*).

The relative density of the samples of perchloric acid to be analyzed was determined using a precision type of Foulk chain hydrometer previously described (*5*). The two reference samples by analysis were 73.49 and 73.51 per cent, average 73.50 per cent, perchloric acid, and 73.69 and 73.71 per cent, average 73.70 per cent, perchloric acid. The chain hydrometer float position differed in equilibrium with these two reference solutions from reading 60 to reading 150 on a millimeter scale. Thus each displacement of 1 mm. in the position of the chain hydrometer float corresponded to $\frac{0.20}{90}$ or 0.0022 per cent change in acidity in the sample being analyzed. The analysis of the samples of perchloric acid intended to represent standard material is given in Table III.

Table III—Analysis of Perchloric Acid by Graphical Interpolation of Relative Densities

Sample	Preparation Pressure	Hydrometer Reading	Calcd. $HClO_4$
	Mm. Hg	*Mm.*	%
Ref. No. 1			73.50 (by analysis)
Ref. No. 2			73.70 (by analysis)
1	3.5–5.0	97	73.58
2	3.5–5.0	102	73.59
3	3.5–5.0	120	73.63
4	3.5–5.0	99	73.58
5	2.2	91	73.57
6	6.5–7.0	100	73.59
		Mean	73.59

By reference to this table it will be seen that if the pressure range 3.5 to 5.0 mm. is maintained, the average strength of the perchloric acid, obtained by distillation of approximately 72 per cent perchloric acid in the apparatus described, results in the preparation of perchloric acid of composition 73.60 per cent. This value is obtained if the distillate from the last 50 per cent of the distillation is taken. At pressures between 2 mm. and 7 mm. the variations in percentage composition of the perchloric acid obtained is inappreciable. It is at once apparent that slight variations in the pressure during distillation or slight inaccuracies in the reading of the pressure-recording device are of no appreciable influence upon the composition of the final product.

Specific Gravity of 73.60 Per Cent Perchloric Acid

Relative density measurements only were required for the purpose of this investigation. The determination of the specific gravity of 73.60 per cent perchloric acid gives 1.71282 at 25°/4° C. The ideal pressure for the distillation of 73.60 per cent perchloric acid has been shown to be 5.7 mm. (*3*).

Summary of Directions for Preparation of 73.60 Per Cent Perchloric Acid

Pure 72 per cent perchloric acid is distilled under a vacuum of 2 to 7 mm. in an apparatus described in Figure 1. When

one-half of the product has been distilled the process is discontinued and the distillate set aside. A clean dry receiver is then used to collect the second fraction distilled under the same conditions. The pressure may vary between the limits given. A pressure of 5 to 6 mm. is best and most easily obtained. The rate of distillation is of no consequence and the temperature varies between 60° and 95° C. depending upon the rate of application of heat. The product obtained by this process varies ± 0.03 per cent in acid content and ± 0.0004 in specific gravity.

If the starting material is 71 per cent perchloric acid the conditions are the same except that 60 per cent is distilled and discarded. Starting with 70 per cent perchloric acid 65 per cent of the distillate is discarded.

Perchloric acid of this standard strength is slightly hygroscopic and fumes very faintly. It should be weighed with the usual precautions to prevent absorbing atmospheric moisture.

To prepare a solution of normal perchloric acid using the product obtained in the manner described a sample weighing 136.4201 grams (using brass weights and assuming average humidity and temperature) is weighed and diluted to 1000 cc.

Comparison of Preparation of Constant Boiling Hydrochloric Acid with That of Standard Perchloric Acid

The preparation of standard perchloric acid can be compared with the preparation of constant boiling hydrochloric acid in the following manner:

The pressure of distillation must be known in the case of hydrochloric acid and the use of a barometer is required. With perchloric acid the pressure may vary over the range 2 to 7 mm. and a very simple pressure-recording device may be used and the barometer eliminated. The preparation of constant boiling hydrochloric acid must be carefully controlled as regards the rate of distillation and prevention of bumping. The perchloric acid process does not vary with the rate of distillation which may be twice as great as in the former process, and the distillation is free from ebullition.

One cubic centimeter of 73.60 per cent perchloric acid (sp. gr. 1.71) equals 2 cc. of constant boiling hydrochloric acid in equivalents of acid contained. Since perchloric acid can be distilled by the process just described at twice as great a rate, and since 50 per cent of the starting product is obtained in comparison with 25 per cent for the hydrochloric acid, the yield of perchloric acid obtained in a given time as compared to hydrochloric acid may be as much as eight times as large.

Literature Cited

(1) Emster, van, *Z. anorg. Chem.*, **52**, 270 (1907).
(2) Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923).
(3) Goehler and Smith, Ind. Eng. Chem., Anal. Ed., **2**, 48 (1931).
(4) Goodwin and Walker, *Trans. Am. Electrochem. Soc.*, **40**, 157 (1922).
(5) Koch and Smith, Ind. Eng. Chem., Anal. Ed., **2**, 41 (1930).
(6) Lubs and Clark, *J. Wash. Acad. Sci.*, **5**, 609 (1915); **6**, 481 (1916).
(7) Smith, Ind. Eng. Chem., **18**, 1216 (1926).
(8) Willard, *J. Am. Chem. Soc.*, **34**, 1480 (1912).
(9) Wyk, van, *Z. anorg. Chem.*, **32**, 115 (1902); **48**, 1 (1905).

Dissociation of Concentrated Perchloric Acid during Vacuum Distillation at Moderately Low Pressures[1]

New Method for the Preparation of Anhydrous Perchloric Acid

O. E. Goehler and G. Frederick Smith

Department of Chemistry, University of Illinois, Urbana, Ill.

A study of the vacuum distillation of 73.3 to 73.6 per cent perchloric acid has been made over the pressure range 7 to 18 mm. and an apparatus described for the preparation of anhydrous perchloric acid in yields of 7 to 10 per cent of the weight of the starting product.

The anhydrous perchloric acid formed is shown to be more stable than that prepared by use of previously known processes.

The mechanism of the distillation described is explained, and this explanation found to be dependent upon the implied existence of a surface film of oxonium perchlorate (OH_3ClO_4).

The following description has for its object the study of the nature of the process and products formed during the vacuum distillation of concentrated perchloric acid in the pressure range 8 to 18 mm. Perchloric acid of approximately the composition of the dihydrate ($HClO_4.2H_2O$, 73.6 per cent acidity) will be shown under the conditions named to undergo a set of dissociations formerly little known. An attempt to explain the mechanism of these dissociations will be made and the design of a special still particularly well adapted to such a study will be described. Under suitable conditions this process serves as a new method for the formation of anhydrous perchloric acid in somewhat small but satisfactory yields. The dissociation reactions involved are represented as follows:

$$4HClO_4{\cdot}2H_2O \longrightarrow 2HClO_4{\cdot}3H_2O + 2OH_3ClO_4 \quad (1)$$
$$2OH_3ClO_4 \longrightarrow HClO_4{\cdot}2H_2O + HClO_4 \text{ (anhyd.)} \quad (2)$$

The procedure employed constitutes the only distillation method known requiring no desiccating agent to accomplish this dehydration. A further distinctive feature consists in the minimum of hazard involved in the preparation of explosive anhydrous perchloric acid.

Historical Data

The first important study of anhydrous perchloric acid and its monohydrate was made by Roscoe (*2*). The existence of a constant boiling mixture with water (72.4 per cent at 760 mm., b. p. 203° C.) was shown. The anhydrous acid was prepared by the reaction between potassium perchlorate and 95 per cent sulfuric acid and by the distillation of constant boiling perchloric acid with 95 per cent sulfuric acid at 110° C. Perchloric acid monohydrate was prepared by dilution of the anhydrous acid with water or strong perchloric acid. This crystalline perchloric acid monohydrate at 100° C. gives a distillate of anhydrous acid and a residue corresponding to the composition of the dihydrate.

A more comprehensive research on the identification cryoscopically of the various hydrates of perchloric acid was made by van Wyk (*5*). The following hydrates were studied:

[1] Received August 23, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930. A portion of a thesis presented by O. E. Goehler in partial fulfilment of the requirements for the degree of doctor of philosophy in the Graduate School of the University of Illinois.

Hydrate	Melting Point °C.
$HClO_4$ (anhy.)	−112
$HClO_4 \cdot H_2O$	+ 50
$HClO_4 \cdot 2H_2O$	− 17.8
$2HClO_4 \cdot 5H_2O$	− 29.8
$HClO_4 \cdot 3H_2O$:	
Alpha	− 37
Beta	− 43.2
$2HClO_4 \cdot 7H_2O$	− 41.4

In the present discussion, for the sake of simplicity, any hydrate higher than the dihydrate will be designated as the trihydrate.

Special Properties Associated with Vacuum Distillation of Perchloric Acid

The vacuum distillation of concentrated (71 per cent) perchloric acid or of the approximate constant boiling composition (72.4 per cent at 760 mm.) up to the composition of the dihydrate (73.6 per cent) shows the distinctive features described in another paper (*3*). For a correct understanding of the present paper the former should be consulted. Under the conditions of vacuum distillation described below, the perchloric acid being distilled is not in simple equilibrium with the vapors formed. An attempt to explain the pronounced tendency of distilling perchloric to superheat is a secondary objective of the present work.

Preparation of Materials and Apparatus Design

Perchloric acid, 70 to 72 per cent, was purchased from the usual sources. The approximate dihydrate of perchloric acid (composition 73.6 per cent) was prepared by vacuum distillation of the former product discarding all but the last 35 per cent of the distillate.

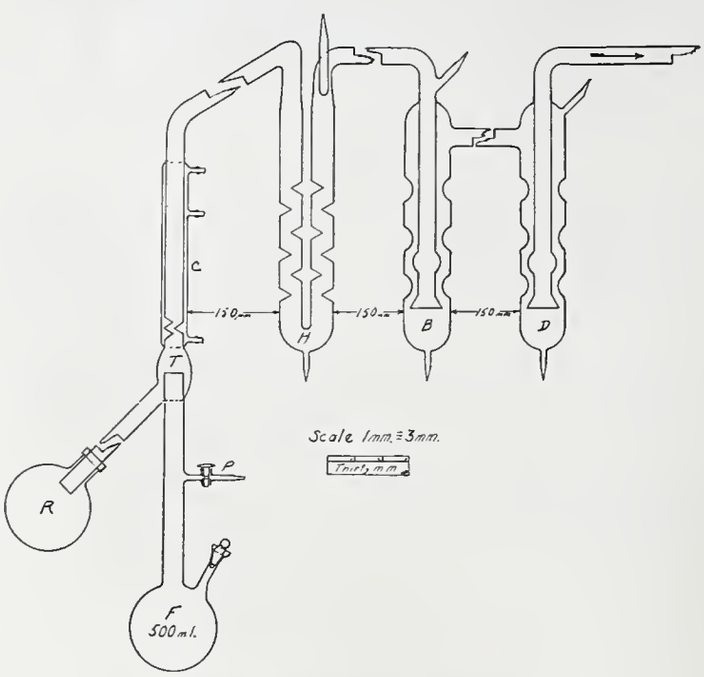


Figure 1—Distillation Apparatus

The distillation apparatus is shown in Figure 1 drawn to scale, and in Figure 2 set up ready for use. Distilling flask *F* is provided with receiver flask *R*, reflux condenser *C*, and reflux trap *T*, to by-pass condensate from *C* into *R*. A train of three joining liquid air traps (shown without Dewar flasks adjusted) are designated *H*, *B*, and *D*. Each liquid air trap is provided with sealed off intake and efflux tubes to provide for recovery of the products obtained. Liquid air trap *D* connects directly to a good rotary oil pump of generous capacity (a megavac pump) by means of rubber pressure tubing. A closed tube differential mercury manometer (not shown) is inserted in this portion of the line. This manometer had been previously checked for accuracy against a McLeod gage. Adjustments in the pressure of the distillation are made by opening stopcock *P* connected with a high-grade drying agent (anhydrone—granular anhydrous magnesium perchlorate). Thermometers for determining the temperature of the distilling liquid and vapors are supported by the stopper of flask *F* which is of the liquid seal type, moist with perchloric acid. Flask *R* is attached using a one hole rubber stopper. Flask *F* is heated by the use of a burner. Condenser *C* is cooled using tap water. No capillary air inlet to *F* is needed.

Distillation Operation

Flask *F* is charged with 250 to 350 grams of 73.4 to 73.6 per cent perchloric acid and the system evacuated to 2 to 5 mm. pressure. A 3 to 4 inch (7.6 to 10.2 cm.) flame from a Bunsen burner is then applied and at 75° to 85° C., depending upon the pressure, vapors of the dihydrate pass into condenser *C*, condense and reflux into *R*. When 15 to 20 cc. of distillate have been collected the operation is discontinued and the flask *R* emptied, dried, and replaced. The purpose of this preliminary operation is to prepare the distilling liquid for the treatment at the higher pressures and consequent greater degree of superheating. During the preliminary distillation, unless the acid is previously chilled, a slight degree of ebullition will result until dissolved gases are expelled. In this case some monohydrate may form in the vessels of the condenser. Some few trial runs are advisable to familiarize one with these operations.

The distillation is now carried out at pressures varying from 8 to 18 mm. within a 1-mm. maximum variation for any individual run. The pressure adjustment is easily made through use of a stopcock *P* if the oil pump has sufficient capacity. The traps *H*, *B*, and *D* are immersed in liquid air and the cooling water in *C* adjusted in rate of flow sufficient to cause a slight deposition of crystals of monohydrate (OH_3ClO_4) at its extreme upper end. These crystals must be maintained in the condenser during the whole distillation process. Perchloric acid dihydrate and trihydrate condense in *C* and reflux into *R* at the rate of 2 to 4 cc. per minute depending upon the degree of superheating. Anhydrous perchloric acid collects in the trap *H* (with a small amount of monohydrate), in trap *B*, and a few cubic centimeters in trap *D*. The yield of anhydrous perchloric acid is highest in the case of the greatest degree of superheating obtained at the higher pressure of distillation. A favored working range is between 12 and 15 mm.

The sampling and analyses necessary for following the various dissociations obtained are accomplished as follows: The distillation is discontinued and the pressure increased to atmospheric. The Dewar flasks containing the liquid air for traps *H*, *B*, and *D* (Figure 1) are removed and the frozen contents on the side walls allowed to melt and run to the bottom of the trap. The frost is then removed from the outside of the traps and the liquid air replaced over the level of the melted acid in the bottom of the trap until it is again frozen. The drawn-out extensions of the traps *H*, *B*, and *D* are then file-marked and broken open before the acid is melted within, and a tube containing a weighed portion of previously analyzed perchloric acid of 72 to 73 per cent acidity is placed in a position to mix with the anhydrous perchloric acid which quickly melts and runs into the absorbing acid.

By previously analyzing and weighing the absorbing acid followed by analysis of the solution obtained from the addition of the known weight of anhydrous acid, the strength of the absorbed acid can be calculated. The absorbing acid

Table I—Distillation of Perchloric Acid Dihydrate at 7 to 18 mm. Pressure in Preparation of Anhydrous Perchloric Acid

Pressure	Concn. of Acids in Flasks Start, F	R	Residue, F	Temperature of Distillation	Amount Distilled	Total Distilled	Anhydrous Acid	Yield $HClO_4$ (Anhydrous)	
Mm.	%	%	%	° *C.*	*Grams*	*Grams*	*Grams*	%	%
16–17	73.4	72.26	73.05	110–117	474.0	276.0	16.4	98	8.7
17.5–18	73.30	71.32	73.05	109–120	285.1	267.9	19.3	97	10.6
17–17.5	73.45	71.86	73.01	108–119	302.0	216.9	13.7	99	9.3
7–7.5	73.35	72.83	73.30	95–102	251.7	203.1	2.9	100	1.9
9–9.5	73.45	72.53	73.40	100–110	204.9	155.4	6.2	97	5.5

should be in sufficient quantity of such strength that the resulting acid concentration of the mixture shall not be greater than 77 or 78 per cent for the reason that above this strength the crystals of monohydrated perchloric acid are not soluble at room temperature. The sampling of the residue in flask *F* and receiver *R* is obviously easily accomplished. That the anhydrous acid obtained was not chlorine heptoxide (*1*), which would not be apparent by the method of analysis described, was proved by its greater chemical activity, freezing point, and other physical properties. Two representative preparations of anhydrous perchloric acid are recorded in Table I.

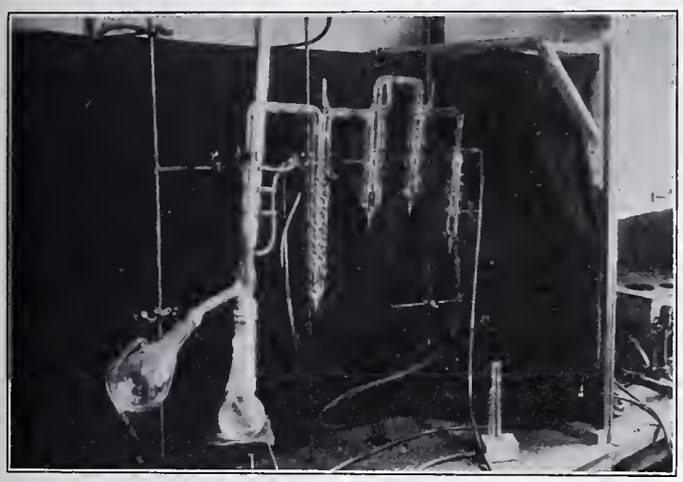


Figure 2—Set-up of Apparatus

From an examination of this table it is observed that the strength of the acid of the distillate has decreased as well as that of the residue left in flask *F*. Both of these results would be predicted to accompany Reaction 1 previously cited. A decrease in acidity for the residue in the distilling flask indicates that the dissociation of Reaction 1 takes place in great part in the liquid phase during the process of distillation. The dissociation of Reaction 2 resulting in the formation of anhydrous perchloric acid from the monohydrate is known to result at temperatures reached by the distillation under the pressures employed (*5*). The separation of the anhydrous acid in the vapor phase in the presence of higher concentrations of the dihydrate and trihydrate is due to the influx of dry air through the water condenser. The hydration of the anhydrous acid in contact with the higher hydrates of the vapor phase is thus prevented. That this reaction would result is shown by the formation of crystals of the monohydrate in the top of the water-cooled condenser. The rate of cooling in the water condenser is adjusted to maintain the conditions leading to the accumulation of the greatest yield of anhydrous acid. An even more completely anhydrous perchloric acid could be obtained if the cooling water of the water condenser were so adjusted as to result in the formation of the deposit of crystals of the monohydrate at a point further down in the condenser tube, but the yield of anhydrous acid would be lower.

The data of Table I show that a larger yield of anhydrous acid is obtained in the case of the higher pressures. However, experiments were made in which the air leak to the flask *R* remained at 8 to 8.5 mm., while the total pressure on the system was increased by means of a stopcock near the pump side of the system. The results show a slight increase in yield of anhydrous acid at the higher pressure but the data showed a decrease in yield as compared to the previously described adjustment of pressure (9–10 per cent yield dropped to 5–6 per cent working at 16–18 mm.).

Possible Explanation of Phenomenon of Superheating

Two characteristics of the dissociation Reactions 1 and 2 for which explanation is desirable are as follows: First, the explanation of the dehydration of perchloric acid accomplished without the presence of a drying agent. Second, the mechanism of the distillation operation accompanied by superheating to such an abnormal extent. It is possible that both these results are explained in the same manner.

The dissociation of perchloric acid dihydrate to form the trihydrate and monohydrate (Reaction 1) under ordinary conditions requires a drying agent of the efficiency of sulfuric acid. The dehydration of strong perchloric acid can be brought about by distillation in the presence of concentrated sulfuric acid with the formation of perchloric acid monohydrate (*1*). While hot concentrated perchloric acid is an efficient drying agent it would be contrary to ordinary experience that the higher hydrates of a given material should be capable of generating a lower hydrate of the same material.

Perchloric acid monohydrate has been shown (*4*) to be in reality of an oxonium structure. The formation of oxonium perchlorate according to the reaction

$$2HClO_4{\cdot}2H_2O = OH_3ClO_4 + HClO_4{\cdot}3H_2O$$

might account for a surface orientation of molecules of oxonium perchlorate which would account for the property of superheating. The retarded liberation of the vapors of the main product of the distillation $HClO_4{\cdot}2H_2O$ as well as the trihydrate of perchloric acid would seem by this mechanism to be explained. That this explanation is plausible is evident from the fact that monohydrated perchloric acid at 110° C. (approximately) is known to dissociate into the dihydrate and anhydrous perchloric acid.

As the oxonium perchlorate molecules dissociate at the surface of the distilling liquid, more assume their position to maintain the surface film and the superheated condition. The temperature of the vapors of the lower hydrates of perchloric acid forced through the surface film of oxonium perchlorate at the temperatures required (110° to 120° C.) do not react to hydrate the anhydrous perchloric acid in the vapors at this temperature.

That this is true is shown by the fact that when a permanent gas is admitted into these mixed vapors, the mean free path of the molecules is decreased to such an extent that the anhydrous acid molecules do not react as a whole with the lower hydrates at the lower temperatures of the condenser, nor do they come in contact with the lower hydrated condenser surface. The anhydrous acid does not condense on the first impact with a cold surface because the three liquid air traps, *A*, *B*, and *C*, are necessary to remove all the anhydrous acid from the air stream. All of the lower hydrates are removed by the water condenser which reflux into receiver *R*.

The anhydrous perchloric acid formed is more stable than this product is generally reputed to be. A sample stored under the prevailing outdoor temperatures of the late winter

season did not explode for approximately two months. A sample could be stored at liquid air temperatures indefinitely without spontaneous decomposition, as shown by the fact that it does not form the usual accumulation of colored decomposition products which after sufficient accumulation bring about the explosion of the sample. A sample was stored in liquid air for 2 months with no decoloration and only exploded after subsequent exposure to room temperature for 4 weeks.

If samples of perchloric acid of greater strength than the dihydrate are desired, the monohydrate may be formed by the solution of the anhydrous acid to the point at which the product solidifies. This concentration of perchloric acid can be stored indefinitely without hazard. It must be kept in mind, however, that even though the process just described for the preparation of anhydrous perchloric acid is entirely without hazard if directions are followed closely, the handling of the product once formed may result in the most violent explosions if it is attempted to store it beyond the point of the formation of an amber color or in case it is allowed to come into contact with organic matter such as dry wood, paper, rubber, cork, cotton, etc.

Literature Cited

(1) Michael and Cohn, *J. Am. Chem. Soc.*, **23**, 444 (1900).
(2) Roscoe, *J. Chem. Soc.*, **16**, 82 (1863).
(3) Smith and Goehler, Ind. Eng. Chem., Anal. Ed., **2**, 48 (1931).
(4) Volmer, *Ann.*, **440**, 200 (1924).
(5) Wyk, van, *Z. anorg. Chem.*, **48**, 1 (1906).

Oxonium Structure of Hydrated Perchloric Acid[1]

G. Frederick Smith and O. E. Goehler

Department of Chemistry, University of Illinois, Urbana, Ill.

Evidence has been supplied substantiating the oxonium structure of form of perchloric acid melting at 50° C., a conclusion previously demonstrated by others.

The exact melting point of oxonium perchlorate has been determined and found to be 49.905° + 0.005° C.

A new form of perchloric acid, oxonium perchlorate monohydrate, is postulated based upon the transition $HClO_4 \cdot 2H_2O = OH_3ClO_4 \cdot H_2O$. The alpha and beta forms of the trihydrate of perchloric acid previously known are likewise postulated to result from the transition $HClO_4 \cdot 3H_2O = OH_3ClO_4 \cdot 2H_2O$. The oxonium structure of all the known hydrates of perchloric acid is therefore indicated as a natural conclusion from the data shown.

The use of the data of this paper has been suggested for the construction of a density–acid concentration table, the analyses for which have been provided by physical rather than chemical means.

The cryoscopic study of the system water–perchloric acid has been made by van Wyk (*7*) over the range H_2O–100 per cent $HClO_4$ with the investigation among other hydrates of the mono-, di-, and trihydrates. The melting point of the monohydrate was found to be 50° C. and of the dihydrate −17.8° C. Two forms of the trihydrate were found, the alpha form, m. p. −37° C., and the beta form, m. p. −43.2° C. In addition to these hydrates the two following forms were shown: $2HClO_4 \cdot 5H_2O$, m. p. −29.8° C., and $2HClO_4 \cdot 7H_2O$, m. p. −41.4° C. The freezing point of anhydrous perchloric acid has been found to be −112° C.

The great difference in the chemical and physical properties of anhydrous perchloric acid and its monohydrate has been explained on the assumption that the hydrate melting at 50° C. is in reality of the oxonium structure, OH_3ClO_4, rather than the simple monohydrated form of perchloric acid. This explanation of Hofmann has been studied experimentally by Volmer (*6*) who demonstrated that the x-ray lattices of the hydrate of perchloric acid m. p. 50° C. and ammonium perchlorate are practically identical. The Hofmann conclusion has, therefore, been rather satisfactorily substantiated and the Hantzsch theory of electrolytes likewise strengthened.

The object of the present investigation was originally the analysis of strong perchloric acid solutions by physical means through the more exact determination of the melting point of perchloric acid dihydrate and the simultaneous determination of its density. Since the relationship between the density and acidity of strong solutions of perchloric acid has been shown to be linear (*7*) the analysis in the region of the dihydrate could then be found with the density determination and a determination of the relationship, per cent acidity equals a function of the change in density. A second reference point in the density–percentage composition curve could then be established by determination of the physical constants of the monohydrate.[2]

The exact determination of the melting point of perchloric acid dihydrate was found to be complicated by the difficulty that a physical transformation (Reaction 2) apparently always takes place upon crystallization of a solution of perchloric acid of practically the correct acid composition 73.6 per cent $HClO_4$. The object of the present paper then became the use of this transition to further substantiate the oxonium structure of the hydrated perchloric acids other than the 50° melting form studied by Volmer. In thus strengthening the Hofmann conclusions as carried out in the x-ray studies of Volmer, it then became necessary to determine the exact melting point of oxonium perchlorate for the purpose of studying transition of Reaction 1. A secondary objective consisted in the explanation of the structure of the previously known alpha and beta forms of the trihydrate of perchloric acid (*7*) which is represented in Reaction 3.

$$OH_3ClO_4 \longrightarrow HClO_4 \cdot H_2O \quad (1)$$
$$HClO_4 \cdot 2H_2O \longrightarrow OH_3ClO_4 \cdot H_2O \quad (2)$$
$$HClO_4 \cdot 3H_2O \longrightarrow OH_3ClO_4 \cdot 2H_2O \quad (3)$$

As a result of this investigation Reaction 1 was not found to take place. Reaction 2 was indicated and Reaction 3 was previously shown (*7*). It naturally follows that the two hydrates of the form $2HClO_4 \cdot 5H_2O$ and $2HClO_4 \cdot 7H_2O$ probably exist in the form $2OH_3ClO_4 \cdot 3H_2O$ and $2OH_3ClO_4 \cdot 5H_2O$. In other words the oxonium structure of hydrated perchloric acids in general is thus indicated.

[1] Received August 23, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] The exact chemical analysis of perchloric acid solutions is not practicable for the reason that a satisfactory reducing agent has not been found capable of forming hydrochloric acid which could then be compared with silver in the usual manner.

Transition of Crystalline Perchloric Acid Obtained at Freezing Point of Approximate 73.60 Per Cent Solution

The apparatus employed followed the design of Beckman (*1*) and of Kanolt (*4*) illustrated in Figure 1 drawn to the scale indicated. The large Dewar flask, *E*, served as the reservoir for a sulfuric acid–ice freezing mixture maintained at a temperature of −19° to −20° C. A partially evacuated Dewar, *D*, served as the jacket for the reaction chamber, *C*, containing the perchloric acid of the determination. Provision was made for the mechanical stirring of the freezing mixture using a platinum wire stirrer, *S*, moving with a period of 40 to 50 strokes per minute inserted through *B*. The freezing of the sample being examined was followed by use of a 10-junction thermocouple made in the conventional fashion from number 28 wire. The freezing mixture could be seeded out through *A* using a small capillary tube dipped in the acid used and frozen by brief immersion in liquid air. A stream of dry air was passed into tubes *A* and *B* to prevent contamination of the sample by atmospheric moisture. The whole cryoscopic bath was insulated from changes in temperature due to outside influences by use of wool felt coverings.

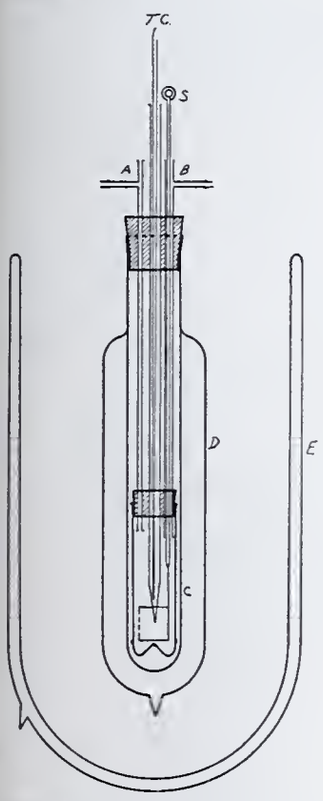


Figure 1—Apparatus for Crystallization of Perchloric Acid

The thermocouple was calibrated at the freezing point of very pure mercury using the value −38.87° C. The deviation from a standard thermocouple was found to be +0.00192 microvolts (*3*). A White single potentiometer was used for recording the temperature provided with a compensating resistance equal to that of the thermocouple. The standard cell used (1.0183 volts at 25° C.) was calibrated against a Bureau of Standards cell. The galvanometer was by Leeds and Northrup having a 5-second period, a sensitivity of 5 mm. per microvolt employing a critical damping of 72 ohms. The image from the galvanometer mirror was cast upon a wall at a distance of 18 feet giving a deflection of 13 mm. per microvolt.

The experimental procedure was as follows: Twenty cubic centimeters of perchloric acid varying in composition 72.3 to 73.8 per cent were placed in the freezing point tube, *C*, and the whole cooled by immersion in a carbon-dioxide-snow cooling chamber. After the acid was undercooled 1 to 2 degrees below its freezing point it was transferred to the vacuum chamber, *D*, immersed in the Dewar flask, *E*, containing the sulfuric acid–ice mixture at a temperature of 1 to 4 degrees above the freezing point of the perchloric acid being examined. The temperature of the well-stirred perchloric acid at this point was followed closely to observe the point of gradual rise in temperature, at which point it was seeded as previously described. The crystallization began at this point and a rise in temperature resulted which reached a variable high point, and instead of the temperature reaching a fixed maximum corresponding to the melting point of the dihydrate and remaining stationary for a fixed interval of time, it began to fall in a direction contrary to the direction of the bath temperature. At the point at which the last crystal disappeared in the solution, the temperature then mounted to the bath temperature. The time-temperature plot is shown in Figure 2.

The examination of Figure 2 representing the composite data for many duplicate determinations of a given sample shows the similarity in behavior in all cases. The general trend of the data shows that the crystal form first produced by the seeding of the undercooled perchloric acid undergoes a transition before the melting point of this form is reached at *B*. The transition takes place with the absorption of heat and is complete before the lower melting point is reached at some point lower than *A*. Reaction 2 above is, therefore, indicated with the stable form represented by the formula $OH_3ClO_4 \cdot H_2O$ (oxonium perchlorate monohydrate). That this form is obtained with the absorption of energy is in accordance with the explanation of the decomposition of perchloric acid of the same composition at approximately 18 mm. and 115° C. in the formation of anhydrous perchloric acid and previously shown (*2*). The dehydration of oxonium perchlorate monohydrate to form oxonium perchlorate according to this explanation was accompanied by the absorption of energy.

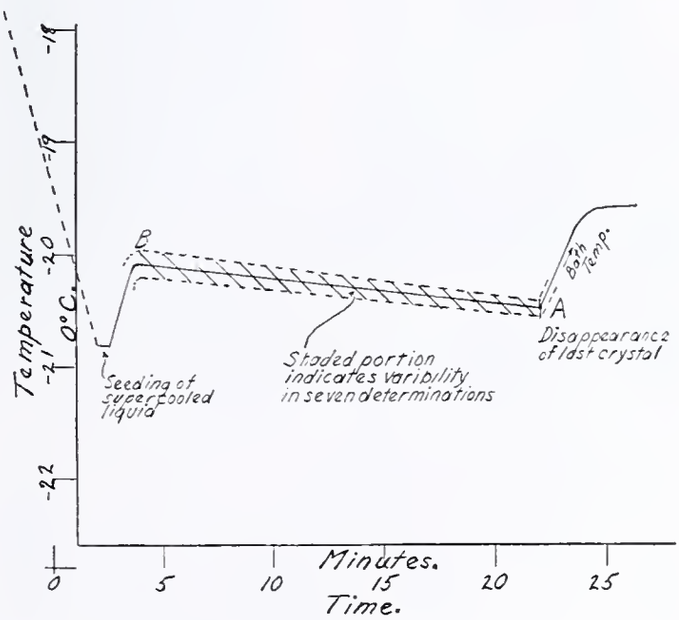


Figure 2—Time-Temperature Plot for Several Determinations

Following the same explanation the beta form of perchloric acid trihydrate previously described (*7*) is to be correctly termed oxonium perchlorate dihydrate since the latter form results from the former with the consumption of energy. The repetition of the freezing point determination of various perchloric acid samples gave results of the same general type. These data are given in Table I.

Table I—Maximum and Minimum Transition Temperatures for Various Strengths of Approximately 73 Per Cent Perchloric Acid

Perchloric Acid	Temperature of Transition Maximum	Minimum
%	° C.	° C.
73.8	−19.11	−19.53
73.4	−19.97	−20.14
73.2	−17.85	−19.34
72.3	−19.40	−20.01

Determination of Melting Point of Oxonium Perchlorate

The determination of the melting point of oxonium perchlorate would serve a twofold purpose in connection with the present investigation. The possible transition of Reaction 1 above would be examined. Previous determination

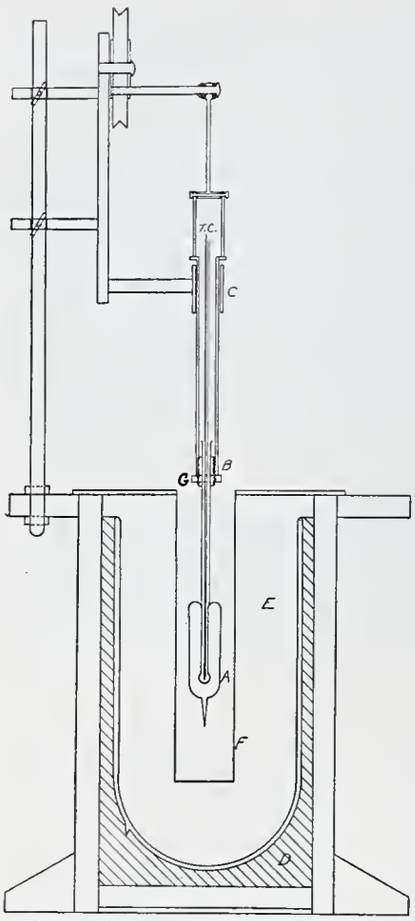


Figure 3—Apparatus for Determination of Melting Point of Oxonium Perchlorate

of the melting point of the 50° melting hydrate of perchloric acid indicated no transition and therefore the nonexistence of perchloric acid monohydrate ($HClO_4 \cdot H_2O$) as subsequently indicated by Volmer. Secondly, the determination of the maximum freezing point for perchloric acid–water system would establish the exact composition of perchloric acid by physical rather than chemical means. The solution of definite weights of oxonium perchlorate in known weights of water together with the determination of the density of such solutions would serve admirably for the establishment of an acid composition–density chart over the range of acid composition between 70 and 80 per cent including the determination of the physical constants for the exact dihydrate of perchloric acid. The latter method of attack is thus substituted for the failure to obtain a maximum or minimum melting point for the transition of Reaction 2.

Oxonium Perchlorate Melting Point Apparatus

The apparatus used in the determination of the melting point of oxonium perchlorate is shown in Figure 3. Dewar flask *E* was fitted into the thermostat box, *D*, and heated electrically and the water of the bath agitated using a small stirrer, the heater and agitator not shown in the figure. The reaction cell, *A*, was constructed on the order of a Dewar flask with very small bore for the entrance of the multiple thermocouple, *T.C.* The sample of acid of approximately the correct composition was added to cell *A* through the small opening at the bottom end and sealed for each observation. Cell *A* was agitated by use of the shaking device shown operating at approximately 300 revolutions per minute. The same temperature recording multiple thermocouple and White potentiometer previously described were used. The thermocouple was calibrated using thiophene-free benzene and the boiling point of water.

Preparation of Samples and Determination of Melting Point

Perchloric acid of approximately oxonium perchlorate composition was prepared from pure thrice-distilled perchloric acid of approximately 73.6 per cent composition prepared by the method of Smith and Koch (*5*) followed by the addition of anhydrous perchloric acid made by the method of Goehler and Smith (*2*). The crystalline perchloric acid thus obtained was melted and poured into the reaction chamber, *A*, Figure 3, which was then sealed for determination. If anhydrous perchloric acid is added to form a solution of greater acidity than that of oxonium perchlorate (OH_3ClO_4), the solution darkens upon storage due to decomposition. For this reason solutions less strong than that of the maximum melting point were prepared and subsequently concentrated by the addition of anhydrous perchloric acid. The anhydrous perchloric acid used for this operation was stored in liquid air to prevent its gradual decomposition and subsequent explosion. As the oxonium perchlorate composition was approached starting with less strong acid by addition of anhydrous perchloric acid, the crystalline acid was produced in larger and larger crystals until at the maximum melting point the entire tube consisted of a transparent mass of crystalline acid.

Four duplicate determinations of the melting point were carried out upon each tube. Between each pair of determinations 48 hours were allowed to elapse to show any failure to duplicate determinations. The reaction of the concentration of the acid in a given case required a rather extended period of time. To show that equilibrium was established, one sample was studied over a period of 16 days. After a given determination the sample tube was weighed, the tip broken off, anhydrous acid added, the tube then resealed and weighed. The determination of the melting point of the oxonium perchlorate was carried out by two methods of

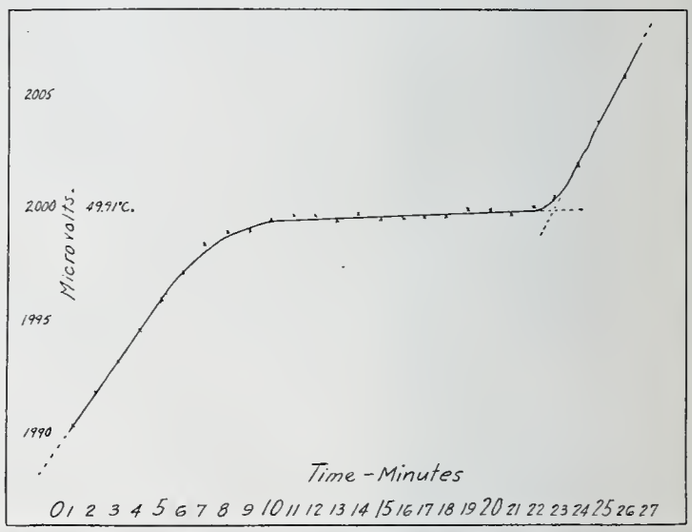


Figure 4—Temperature Record for Typical Runs in Determining Melting Point of Oxonium Perchlorate

application of heat to bring about the melting. In one the bath temperature was maintained at 0.5° to 1.0° above the melting point of the sample and the sample allowed to melt as a result of this higher temperature employed. In the other case the bath temperature was gradually raised to a point equal to and slightly above the melting point of the sample. Both methods gave identical results. A graph of the temperature record for a typical run is shown in Figure 4. The results of the determination of the maximum melting point of a group of individual determinations for three different samples of material are given in Table II.

Table II—Melting Point of Oxonium Perchlorate

Sample	Av. Max. Melting Point ° C.	Max. Deviation of Four Detns. ° C.
1	49.903	0.017
2	49.906	0.023
3	49.910	0.019

Discussion of Results

The results show a satisfactory individual agreement as well as duplicate agreement. Results are expressed to thousandths of a degree although the thermocouple used

does not exceed an accuracy of 0.005° C. The melting point of oxonium perchlorate is thus found to be 49.905° + 0.005° C. No evidence of the transition of Reaction 1 above was found. Perchloric acid monohydrate has not, therefore, been shown to exist and the oxonium structure of perchloric acid of this theoretical composition thus indicated.

Literature Cited

(1) Beckman, *Z. physik. Chem.*, **21**, 239 (1896).
(2) Goehler and Smith, Ind. Eng. Chem., Anal. Ed., **3**, 55 (1931).
(3) International Critical Tables, Vol. 1, p. 57.
(4) Kanolt, Bur. Standards, *Sci. Paper* **520**.
(5) Smith and Koch, Ind. Eng. Chem., Anal. Ed., **3**, 52 (1931).
(6) Volmer, *Ann.*, **440**, 200 (1924).
(7) Wyk, van, *Z. anorg. Chem.*, **48**, 1 (1906).

Oxonium Perchlorate as Reference Standard for Construction of Specific Gravity–Percentage Composition Table for Strong Perchloric Acid Solutions[1]

G. Frederick Smith and O. E. Goehler

Department of Chemistry, University of Illinois, Urbana, Ill.

Oxonium perchlorate (OH_3ClO_4, m. p. 49.905° C.) is used for the preparation of known strengths of concentrated perchloric acid solutions.

A determination of the density of strong solutions of perchloric acid is described and the construction of a density–acid composition chart over the range 65 to 75 per cent perchloric acid carried out. The determination of the constants used in the calculation of interpolated and extrapolated values is given.

The determination of reference points in the density–acid composition chart established the density of the dihydrate of perchloric acid at 25°/4° C. to be 1.71282. Constant boiling perchloric acid 72.4 per cent at 760 mm. and 203° C. has the approximate density 1.6964.

The chemical analysis of strong solutions of perchloric acid in the region of 65 to 75 per cent acid strength is obtainable only by the application of an indirect method. A reference acidimetric standard is first used to standardize the solution of a base which is then in turn used for the analysis of the perchloric acid solution in question. This indirect analysis is made necessary by the fact that a satisfactory method has not been developed for the reduction of perchlorates to chlorides which could then be determined using silver. The preparation of an accurate density–percentage composition table within the range under question is desirable because concentrating dilute solutions of perchloric acid either at atmospheric pressure or under reduced pressure gives rise to acid within this range of percentage composition. Perchloric acid, when distilled at 760 mm., forms a constant boiling mixture with water which consists of 72.4 per cent acid. The formation of the approximate dihydrate of perchloric acid ($OH_3ClO_4 \cdot H_2O$) which has an acid composition of 73.60 per cent results from the vacuum distillation of perchloric acid of constant boiling strength (*2, 5, 6, 7*).

The object of the present paper is the construction of a density–percentage composition table, the accuracy of which exceeds that of existing data, using a method which can be demonstrated to be superior to such data, and employing methods of chemical analysis only. The method of attack is wholly dependent upon the accuracy with which the melting point of the highest melting hydrate of perchloric acid can be determined (*2*) (OH_3ClO_4, m. p. 49.905° ± 0.005° C.). This product, by consulting the data of van Wyk (*8*) can easily be seen to serve better than any other known form of perchloric acid as a reference point in the analysis of strong perchloric acid following the cryoscopic method, and independent of chemical analysis.

[1] Received August 23, 1930. A portion of a thesis presented by O. E. Goehler in partial fulfilment of the requirements for the degree of doctor of philosophy in the Graduate School of the University of Illinois.

Previous Work

Published work closely related to the present investigation is found in the investigations by van Wyk (*8*), van Emster (*1*), and Hantzsch (*3*). The data of these investigators (recalculated in some cases to gain uniformity for the purpose of easy comparison) as applied to the determination of the density of perchloric acid of strength 73.60 per cent (the dihydrate composition) is given in Table I. The values obtained as hereinafter described are included to conserve space.

Table I—Density of 73.60 Per Cent Perchloric Acid and Related Constants

Investigator	Density 25°/4° C.	Coefficient of Expansion Alpha	Range °C.	n_D^{25}	$d\Delta/dC$
van Emster	1.70942	0.00121	15–30	.....	0.01351
van Wyk	1.7130	0.00121	20–50	.....	0.01390
Hantzsch	1.71299	.....		1.42064	0.01366
Present work	1.71282	0.00122	20–30	1.42052	0.01343

$$\text{Alpha} = \frac{d_1 - d_2}{t_2 - t_1}$$ (change in density per degree change in acid concentration).

Outline of Procedure

Samples of oxonium perchlorate (84.794 per cent $HClO_4$) are prepared by the method of Smith and Goehler and their exact composition and identity determined by the determination of their exact melting point (49.905° C.). Weighed portions of these samples of oxonium perchlorate are then diluted with weighed portions of pure water and a density determination made of the solutions thus prepared. The identity of the density thus found for solutions of the same acidity based upon the dilution of the individual preparations of oxonium perchlorate serves as an additional evaluation of the uniformity in composition of the high melting hydrates as determined by their melting point. Further dilution of the samples thus formed serves for the determination of other points on the density–acid composition curve. From

the data thus accumulated the change in density per interval of change in acid composition is readily calculated and the agreement with a linear function thus examined. The analyses are, therefore, dependent only upon physical observations.

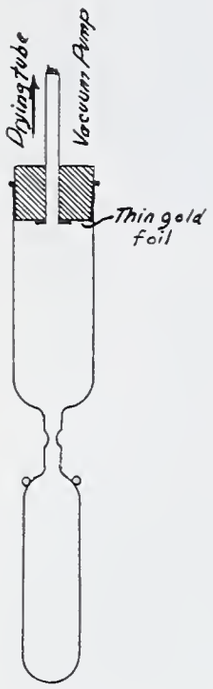


Figure 1—Reaction Tube

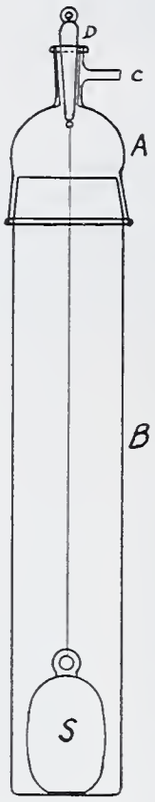


Figure 2—Densimeter Tube

Preparation of Solutions of Known Acid Composition

Oxonium perchlorate prepared as previously described (*2*), having the melting points 49.905° ± 0.005° C., was transferred to the lower portion of the reaction tube shown in Figure 1 in the following manner:

The melting point tube containing the oxonium perchlorate was placed in the upper portion of the reaction tube after the tip was broken to provide for the transfer of the contents. The stopper with a thin gold foil covering is inserted and the whole apparatus dried by evacuating a number of times and refilling with dry air. The whole reaction tube was then immersed in a water bath at 55° C. up to the height of the stopper and the contents of the melting point tube melted and allowed to collect in the lower part of the reaction tube. It was then fused at the constriction, and from the original weight of the tube and the two parts after the transfer of the oxonium perchlorate, the weight of the sample was obtained.

The weighed sample tube of oxonium perchlorate was file-marked at the neck, reweighed, and the tube opened. A weighed quantity of water was then added and the tube resealed. The composition of the resulting acid was then calculated and the density determined. The latter operations were repeated and a new acid concentration and density determined.

Determination of Density of Concentrated Perchloric Acid

The determination of the density of concentrated perchloric acid was carried out following the displacement method described in Bureau of Standards Bulletin 9 (*4*). The balance employed and the arrangement of the suspensions in the present work provided for an accuracy of ± 0.4 mg. Weights were calibrated and the vacuum corrections applied as well as corrections for atmospheric conditions, including psychrometer relative humidity, temperature, and barometric corrections.

The displacement sinker was made of Pyrex glass rod molded into shape, annealed 48 hours at 300° C. to minimize thermal hysteresis, and allowed to age for 10 days. The sinker was suspended by a platinum wire having a diameter of 0.0035 inch dull goldplated over the immersed portion to insure wetting by the perchloric acid and avoiding the phenomena associated with "sticking" which is thus best eliminated.

The densimeter tube is shown in Figure 2 and had two ground glass stoppers, *A* and *D*. Ground joint *A* provided for the introduction of the sinker and sample. Ground joint *D* supported the upper and lower suspensions and was protected against introduction of moist air by use of the side tube, *C*, through which a slow stream of dry air was passed during the period of time in which stopper *D* was disengaged.

The densimeter tube was maintained at a constant temperature with an accuracy of ± 0.01° C. using the large Dewar tube thermostat shown in Figure 3. The water of the thermostat bath was provided with mechanical stirrer, heating coil, and cooling coil, and its temperature was recorded by a Callender platinum resistance thermometer with compensating leads, using a specially designed Wheatstone bridge. The movement of the galvanometer by means of a system of lights and mirrors cast an image on a scale above the balance. By setting the Wheatstone bridge at the properly calculated setting for a given temperature, the bath temperature during measurement was closely controlled by use of a switchboard controlling the heating and cooling coils and stirrer of the thermostat. The platinum resistance thermometer was calibrated at the ice point, the freezing point of mercury, and the boiling point of water.

The volume of the sinkers employed was found to be as follows:

	No. 1	No. 2
Mass, grams	66.3081	21.5544
Volume:		
20° C.	28.5512	
25° C.	28.5528	9.6170
30° C.	28.5545	

Distilled water was used as the calibration liquid and the best values for its expansion with change in temperature. The calculation of the densities determined was made using the following formulation.

$$D\frac{t}{4} = \frac{(S - W) + (Z - Y)}{V_t}, \text{ where}$$

$D\frac{t}{4}$ = density of sample at temperature t
S = relative weight of sinker plus suspension
W = relative weight of sinker in liquid plus suspension
Z and Y = respective vacuum corrections for S and W
V_t = volume of sinker at temperature t

The results of series of determinations of points of reference to be used in the construction of a density–percentage composition chart for concentrated perchloric acid solutions are found in Table II.

Table II—Determinations of Points of Reference Used in Construction of Density–Percentage Composition Chart

Vacuum Wt. $HClO_4$	$HClO_4$	Vacuum Wt. Anhyd. $HClO_4$	Vacuum Wt. $HClO_4 + H_2O$	Resulting $HClO_4$	Density 25°/4° C.	$d\Delta/dC$ [b]
Grams	%	*Grams*	*Grams*	%		
35.3531	84.794[a]	29.9774	41.0190	73.082	1.70583	.....
30.7492	84.794[a]	26.0735	35.6712	73.094	1.70608	.....
40.0530	73.082	29.2715	40.5097	72.257	1.69478	0.01341
40.3712	72.257	29.1710	41.6093	70.107	1.66582	0.01344
41.6093	70.107	29.1710	46.2831	63.027	1.57104	0.01358
35.4381	73.094	25.9031	36.5718	70.828	1.67552	0.01345

[a] Oxonium perchlorate (OH_3ClO_4), m. p. 49.905° ± 0.005° C.
[b] Change in density per degree change in acidity.

From an examination of this table it will be observed that the value for $d\Delta/dC$ (the change in density per unit change in per cent) within the experimental error shows the relationship to be linear over the 70–73 per cent acid concentration, an average value of 0.01343 being obtained. The agreement between the present work and the value obtained by van Emster (*1*) is better than that obtained

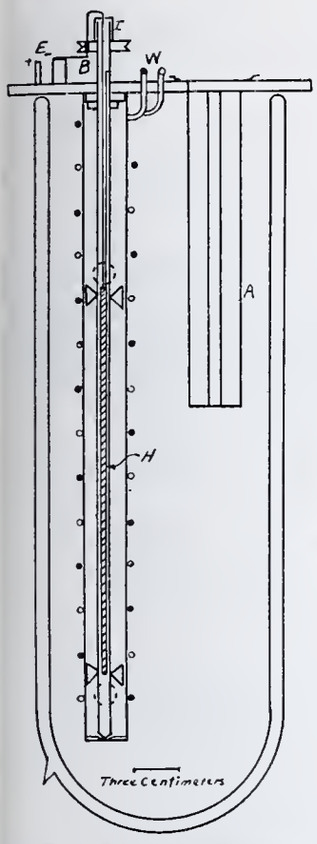


Figure 3—Dewar Tube

by comparison with van Wyk (*6*) or Hantzsch (*3*). The value $d\Delta/dC$, 0.01343, together with the data of Table II, gives for the density of 73.603 per cent $HClO_4$ (the $OH_3ClO_4 \cdot H_2O$ hydrate) the value 1.71282 with a probable accuracy of 5 units in the fifth place of decimals. Here the agreement is closer between the present work and that of van Wyk and Hantzsch. (Compare with Table I.) The determination of the coefficient of expansion resulted in a substantial agreement between the present work and previous observers (*8*, *1*, *3*). Between 63 and 70 per cent acid concentration the value for $d\Delta/dC$ increases slightly.

Construction of Density–Acid Composition Table for 65 to 75 Per Cent Perchloric Acid

The data of Table II serves for the construction of a table of values relating density and acid composition. The values obtained are included in Table III. Values given other than those for the exact multiple of 0.25 per cent in acid composition are the result of actual observation. The remainder are calculated. The values of the density experimental reference points are intended to be accurate to 5 units in the fifth decimal place and the acid composition to within ± 0.01 per cent. Values for the calculation are as follows: $d\Delta/dC$ = 0.01343 between the limits 70 to 75 per cent acid composition, and $d\Delta/dC$ = 0.01351 for the remainder. The calculated values for the density of Table III are thought to be accurate to the fourth decimal place.

Table III—Density and Percentage Composition of 65–75 Per Cent Perchloric Acid

$HClO_4$ %	Density 25°/4° C.	$HClO_4$ %	Density 25°/4° C.	$HClO_4$ %	Density 25°/4° C.	$HClO_4$ %	Density 25°/4° C.
63.027[a]	1.57104	....	.....	71.25	1.68099	...	.....
65.00	1.59665	68.25	1.64055	71.50	1.68434	74.25	1.72124
65.25	1.60002	68.50	1.64393	71.75	1.68774	74.50	1.77458
65.50	1.60340	68.75	1.64731	72.00	1.69106	74.75	1.72791
65.75	1.60678	69.00	1.65060	72.25	1.69442	75.00	1.73125
66.00	1.61016	69.25	1.65406	72.257[a]	1.69478	...	.....
66.25	1.61353	69.50	1.65744	72.50	1.69778	...	.....
66.50	1.61691	69.75	1.66082	72.75	1.70113	...	.....
66.75	1.62029	70.00	1.66420	73.00	1.70449	...	.....
67.00	1.62367	70.107[a]	1.66582	73.082[a]	1.70583	...	.....
67.25	1.62704	70.25	1.66756	73.094[a]	1.70608	...	.....
67.50	1.63042	70.50	1.67092	73.25	1.70785	...	.....
67.75	1.63380	70.75	1.67427	73.50	1.71120	...	.....
68.00	1.63718	70.828[a]	1.67552	73.75	1.71456	...	.....
...	.....	71.00	1.67763	74.00	1.71790	...	.....

a Values experimentally determined.
$d\Delta/dC$ 60–65% = 0.01351
65–75% = 0.01343

Literature Cited

(1) Emster, van, *Z. anorg. Chem.*, **52**, 220 (1907).
(2) Goehler and Smith, Ind. Eng. Chem., Anal. Ed., **3**, 55 (1931).
(3) Hantzsch, *Z. physik. Chem.*, **A 144**, 147 (1929).
(4) Osborne, McKelvey, and Bearce, Bur. Standards, *Bull.* **9**, 328 (1913).
(5) Smith and Goehler, Ind. Eng. Chem., Anal. Ed., **3**, 48 (1931).
(6) Smith and Goehler, *Ibid.*, **3**, 58 (1931).
(7) Smith and Koch, *Ibid.*, **3**, 52 (1931).
(8) Wyk, van, *Z. anorg. Chem.*, **48**, 1 (1906).

An Improved Absorption Tube for Combustion Analysis[1]

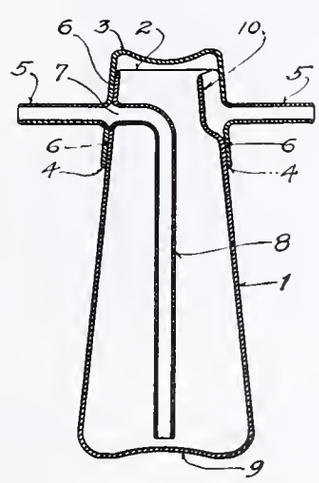
W. D. Turner

Department of Chemical Engineering, Columbia University, New York, N. Y.

SINCE the advent of solid absorbents, such as Ascarite, for combustion analysis, many designs of absorption tubes have been proposed involving more and more advantages over their predecessors; yet none of them possessed at the same time all the refinements of manipulation combined with simplicity of design. To meet this need an apparatus, diagramed in the accompanying illustration, was devised.

The innovation consists in using an external instead of an internal stopper, allowing the cut-off of both openings without the use of return bends or other bypasses. This renders possible a simplification of design with the following advantages:

Minimal outside surface—easy to wipe to constant weight.
Minimal parts—one body, one stopper, one ground joint.
Minimal surface contour—low breakage.
Simple, positive operation—one turn of one stopper shutting inlet and outlet short off. (This was the particular point sought, so that for combustions in oxygen there would be no diffusion of air into the absorber during the operation of disconnecting.)
Minimal waste space—larger capacity completely utilized.
Stable standing.
Light weight.
Plain internal design—surface accessible to wiping.
Ground joint external—not contaminated in charging.
Simple construction—low cost.



Absorption Bottle for Solid Absorbents

Round glass body, 1, 2; external stopper, 3, 4; lateral tubes, 5; ground joint, 6; to tube attached to inner side of body neck, 7, 8; depressed channel communicating with the top interior, 10.

Absorbers of this type have been in satisfactory use in the laboratories of the Bakelite Corporation and at Columbia University, and have been readily made to order by the glass-blowing departments of Eimer and Amend and Columbia University.

[1] Received October 13, 1930.

Fusain[1]

S. W. Parr, H. C. Hopkins, and D. R. Mitchell

University of Illinois, Urbana, Ill.

FUSAIN, or mother-of-coal, is receiving more attention than formerly because of the various properties now being assigned to it. Certain studies in the laboratories at the University of Illinois have developed additional data which afford further information of value.

The bedding planes which are made of fusain are usually very thin but at times may be found in lenses 8 inches in thickness, although such deposits are exceptional. It is generally soft, friable, leaves soot marks on the fingers, and is more or less unconsolidated as compared with the rest of the coal in the bed. Because of the porous character of fusain in its normal state, it affords an easy passageway for infiltrating waters, and such waters, especially in the thicker bands, are very apt to deposit mineral matter from solution. In this way there will naturally result hard and dense layers quite in contrast to the soft friable layers that characterize most of the cleavage planes. These very thin layers are, therefore, usually the most friable and samples of such material can be removed in sufficient amount for analysis by use of care and a good brush.

It is not intended to discuss here the probable origin or method of formation of this material, but some information in that direction, as well as concerning its properties and chemical characteristics, may be gained by making the usual analysis and calculations for indicating the unit volatile and fixed carbon, as well as the unit B. t. u.

Mines were visited and lumps of freshly mined coal were selected containing fusain bands. Three or four lumps were selected from each mine. These samples were further sampled in the laboratory to obtain fusain samples free from other coal constituents, such as bright coal and dull coal. The lumps were broken along the bands of fusain and clean pieces selected, these pieces further broken down, and samples showing the presence of bright or dull coal discarded. Two kinds of fusain were noted during sampling operations, one a much harder variety than the other, and these two kinds were kept separate and are listed in the accompanying table as "soft" or "hard."

Table I—Proximate Analyses of Fusain from Moisture-Free Illinois Coal

Sample	County	Coal Bed	Volatile Matter	Fixed Carbon	Ash	Sulfur	Fuel Value	Unit Coal	Variety Fusain
			%	%	%	%	B. t. u.	B. t. u.	
7	Vermilion	6	23.95	59.20	16.85	5.73	12,080	14,980	Hard
8	Vermilion	7	26.95	54.25	18.90	8.18	11,800	15,100	Hard
9	Vermilion	6	20.75	71.45	7.80	2.58	13,600	15,050	Hard
10	Vermilion	6	13.78	79.24	6.98	1.56	13,710	14,860	Soft
22	Jackson	2	15.79	69.01	15.20	6.57	12,197	14,833	Soft
23	Jackson	2	13.00	80.33	6.67	1.78	13,794	14,913	Soft
25	Jackson	2	18.69	76.86	4.45	0.75	14,165	14,903	Soft
26	Jackson	2	15.22	71.74	13.04	4.75	12,560	14,851	Soft
29	Perry	6	21.04	65.34	13.62	5.97	12,291	14,635	Soft
30	Randolph	6	18.83	68.63	12.54	1.28	12,795	14,837	Hard
31	Jackson	6	18.30	71.80	9.90	0.77	13,295	14,912	Hard
Average			18.74	69.80	11.44	3.63	12,930	14,890	

The accompanying tables give the results of chemical analyses of eleven different samples from different parts of the state, taken from three different coal beds. These results are on a dry or moisture-free basis. One condition of fusain not given in the tables, but calling for reference, is the amount of moisture in the air-dry condition. Coals of the Illinois type when brought to the air-dry condition in the laboratory will contain from 2 to 6 per cent moisture, and the samples of fusain under similar conditions contained from 0.5 to 2.0 per cent moisture. This would be indicative of the porosity of fusain as compared with the bright and dull coal, since it gives up its moisture much more readily and completely than the other banded constituents.

Table II—Unit Volatile Matter

Sample	Unit Volatile Matter	Sample	Unit Volatile Matter
7	27.30	23	19.26
8	31.32	26	15.89
9	21.79	29	22.64
10	15.59	30	21.27
22	16.36	31	20.15
		Average	20.44

The volatile matter percentages were from 15 to 20 per cent lower than is general for the rest of the coal bed. It would appear from the data that the volatile matter of fusain is usually about 20 per cent, and the average for ten samples was found to be 20.44 per cent. Ash percentages range from a low of 4.45 to a high of 18.80 per cent. The statement is frequently made that the fusain of the banded constituents of coal contains more ash than the other bands, but this may not always be true as seen from the above. In fact, it would appear that fusain was originally a high grade low-ash material but, owing to infiltration of impurities because of its porous structure, the ash content was increased. Sulfur percentages follow rather closely the ash percentages—that is, a low-ash fusain is generally low in sulfur and, conversely, a high-ash fusain is generally high in sulfur.

The most striking feature to be noted here is the fairly consistent character of the material, and especially the uniformity of the unit B. t. u. values, considering that samples were taken from all parts of the state as well as from different beds. While the material is non-coking, it has too high and too consistent a volatile constituent to admit of its being the product of fire, as might be inferred from some designations applied to it. One of the striking characteristics of fusain is its absorption of water, and this has been referred to elsewhere as furnishing the mechanism for the slacking of bituminous coals (*2*).

Sinnat (*3*) has devised a method for determining the relative volume of absorption on the part of fusain for water and solutions, as compared with the coal substance with which it is associated. In some tests he found that fusain absorbed over 100 times as much as the coal in the same length of time. It is a well-recognized fact that fusain is unevenly distributed, hence we would expect an uneven absorption of water on the part of samples of coal from the same mine. It also indicates that underground waters will travel the most accessible fusain bands. The deposition of mineral salts which accompanies this process readily accounts for the high ash of some of the fusain bands.

The unit volatile matter, calculated by the method of Parr (*1*), gives the amount of volatile matter in the pure coal substance. The lowest value found is 15.59 and the highest 31.32, with an average of 20.44. However, the chief value of the unit volatile matter content lies in the fact that it would seem to refute completely the forest fire theory for the formation of fusain. The unit volatile matter would certainly be very much lower if fusain were formed because of forest fires sweeping over the coal-forming swamps.

[1] Received August 2, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Fusain is entirely lacking in agglutinating power. No coke-buttons were formed during the determinations for volatile matter. The residue from the crucible is a fine powder with no evidence of any coking tendency.

Table III—Proximate Analyses of Moisture-Free Face Samples from the Same Mines as Fusain Samples of Table I

Sample	County	Coal Bed	Volatile Matter	Fixed Carbon	Ash	Sulfur	Fuel Value	Unit Coal
			%	%	%	%	B. t. u.	B. t. u.
7-*a*	Vermilion	6	40.90	54.45	4.65	2.21	13,555	14,297
8-*a*	Vermilion	7	41.64	49.59	8.77	3.46	12,904	14,310
9-*a*	Vermilion	6	39.35	53.40	7.25	1.70	13,390	14,189
22-*a*	Jackson	2	42.60	52.84	4.56	1.06	13,320	14,039
23-*a*	Jackson	2	33.28	48.58	18.14	3.25	11,577	14,705
25-*a*	Jackson	2	39.69	56.72	3.89	0.75	13,857	14,501
26-*a*	Jackson	2	43.62	52.54	3.84	1.94	13,649	14,295
29-*a*	Perry	6	44.48	44.80	10.72	2.62	12,427	14,231
30-*a*	Randolph	6	43.80	42.43	13.77	2.77	12,103	14,312
31-*a*	Jackson	6	41.49	47.56	10.95	1.06	12,672	14,405
Average			41.08	50.29	8.65	2.08	12,945	14,328

Table III gives some information concerning the coal substance proper, face samples of which were obtained in the usual manner when the fusain samples were taken. A striking difference is shown between the fusain and the total coal values for ash and sulfur. The unit coal B. t. u. values also are consistently higher for fusain. Other analyses of coals from the counties and beds given in this paper may be found in numerous publications of the Engineering Experiment Station, University of Illinois, and in Bulletin 56 of the Illinois State Geological Survey, Urbana, Ill.

The authors wish to emphasize the fact that these results, though meager, may point the way to other investigators and certainly shows the need for further fundamental study of the chemical properties of the various bands common to bituminous coal of the Illinois types—namely, vitrain, or bright coal (anthraxylon), dull coal (attritus), and fusain (mineral charcoal).

Literature Cited

(1) Parr, J. Ind. Eng. Chem., **14**, 921 (1922).
(2) Parr and Mitchell, *Ibid.*, **22**, 1211 (1930).
(3) Sinnat, *Trans. Inst. Mining Eng.*, **62**, 156 (1921).

An Electrically-Heated Melting Point Apparatus[1,2]

Charles E. Sando

Bureau of Chemistry and Soils, United States Department of Agriculture, Washington, D. C.

The apparatus shown in the accompanying illustrations has been used for a number of years with such satisfactory results that its general description seems worth while.

It consists essentially of an electrically-heated modified Thiele-Dennis melting point tube, *A*, a lead container, *B*, filled with sand to prevent damage by sulfuric acid in case of breakage, a lamp, *C*, and a rheostat, *D*, all suitably mounted for convenience and portability in the laboratory.

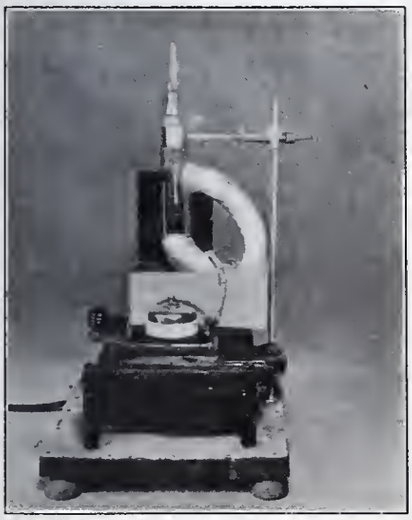


Figure 1—Melting Point Apparatus

The Thiele-Dennis tube is constructed of Pyrex glass and modified by having a smaller tube, *E*, which is closed at the lower end, sealed within the vertical portion, and extends 1 or 2 inches (25.44 or 50.8 cm.) below the point of attachment, *F*, of the side arm. This modified form thus constitutes a combination Roth-Thiele-Dennis apparatus. The side arm, *G*, is wound in the region of its lowest portion with asbestos-covered chromel heating element and insulated with asbestos. The asbestos covering and a portion of the vertical tube are painted with aluminum paint to reduce radiation to the minimum.

Employing a mixture of sulfuric acid and potassium bisulfate as the heating liquid makes it possible to reach a temperature of about 300° C., provided the absorption of moisture by the liquid is prevented by means of a calcium chloride tube at *H* when the apparatus is not in use. With the particular apparatus here illustrated and with a current of 1.4 amperes, about 6 minutes are required to raise the temperature in the inner tube from room temperature to 100° C., about 12 minutes from room temperature to 200° C., and about 25 minutes from room temperature to 300° C. Any desired range in temperature under 300° C., and the rapidity of change from one temperature to another are easily regulated by means of the adjustable rheostat. The melting of the substance itself is plainly observed with the aid of light coming through the small hole in *I* from the lamp *C*.

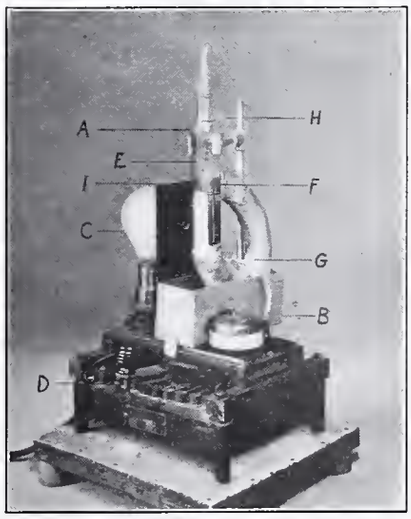


Figure 2—Another View of Melting Point Apparatus

[1] Received October 7, 1930.
[2] Contribution No. 91 from Food Research Division.

Determination of Sulfur by Means of the Turbidimeter[1]

S. W. Parr and W. D. Staley

University of Illinois, Urbana, Ill.

REQUIREMENTS for sulfur determinations under widely varying conditions and in various and complex combinations seem to be on the increase. Not the least noticeable of these conditions is in connection with the work of the power plant where, for some of the determinations, convenience, speed, and a minimum or absence of chemical training are obvious conditions for arriving at the sulfur factor. On many accounts the sulfur photometer or turbidimeter lends itself in an attractive manner to this determination. Such an instrument has been in use for a number of years but the wider scope required for its functioning and the increasing demand for a high degree of accuracy, along with a greater facility of operation, has made it desirable to redesign the apparatus with these particular applications in view.

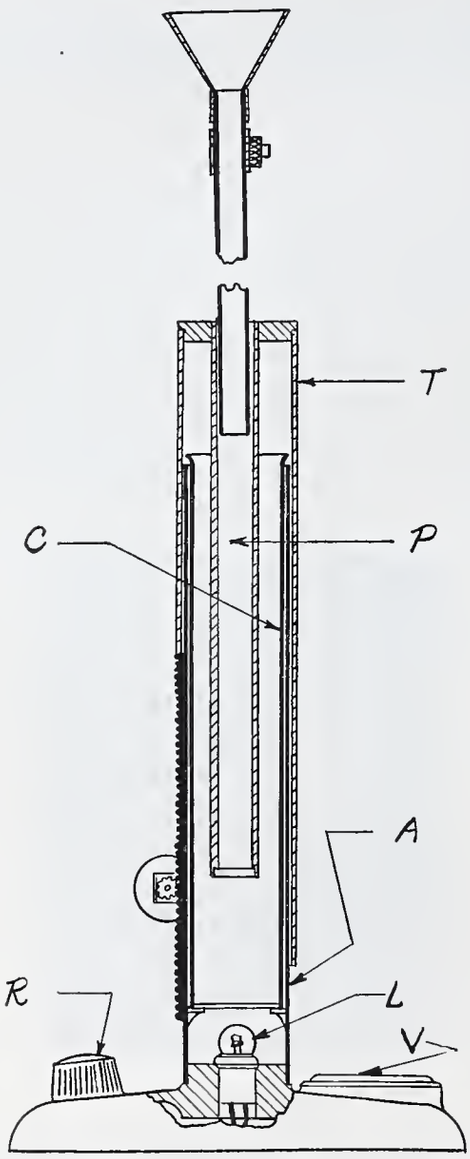


Figure 1—Cross Section of Turbidimeter

[1] Received October 2, 1930. Presented before the Division of Gas and Fuel Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

This extended use is especially notable in connection with the control of sulfates in boiler water, to conform to the A.S.M.E. standard, as a check on the development of embrittlement or cracking of the boiler plates.

Description of Apparatus

In Figure 1, the base supports all of the various parts. A light of about 2 candle power is mounted in the center with the current supplied from two or three dry cells. This current is passed through a voltmeter and also through a resistance, *R*, so that the light can be set at any standard voltage, where it can be retained throughout a test. *A* is a tube which serves as a standard for the other parts of the apparatus. It supports a stationary telescoping tube, *C*, with an optical glass bottom immediately above the light. This tube holds the turbid solution to be tested and also has a plunger tube, *P*, which is empty but which has an optical glass bottom and which may be moved up and down, toward or from the light, by the ratchet. The distance from the optical glass in the bottom of *P* to the optical glass bottom in *C* is measured in millimeters on the scale, *S*.

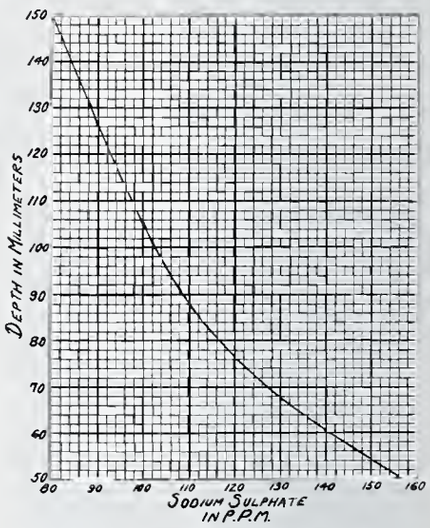


Figure 2—Turbidimetric Reading by Various Operators

The advantages of this arrangement are, that having made up the turbid solution to a standard amount, say 200 cc., the depth of turbidity for the conditions chosen is not disturbed by ripples on the surface of the liquid. Additions of more solution to secure greater depth are obviated. The optical glass is entirely submerged at all stages in the reading, and is moved up or down within the solution to secure the necessary depth and end point. Both tubes are of Bakelite or opaque glass and do not promote diffusion of the light. The eyepiece, located in a favorable position above the instrument, requires that the distance from the eye to the light be the same for all readings. The end point is taken as the complete disappearance of the red filament, which gives a far sharper end point than is possible between a lighter and darker spot of light where both consist of diffused light of varying intensities. By means of the resistance in the voltmeter it is possible to correct the variation in the strength of

the battery so that a light of uniform candle power is always available.

It will be seen at once that the conditions thus secured correct many of the variables inherent in other forms of apparatus of this type. Indeed, the variation in eyes between different operators is reduced to a minimum, as may be seen from Table I. The solutions employed in this test were samples of boiler waters taken from the blow-off at the power plant. Four different persons made readings and the average of three readings for each person was taken. These people were taken at random and operators 3 and 4 were substantially without experience in this sort of work.

Table I—Turbidimetric Readings by Various Operators

Solution	Operator 1	Operator 2	Operator 3	Operator 4
	Mm.	*Mm.*	*Mm.*	*Mm.*
1	126	127	129	132
2	91	84	85	85
3	66	65	65	67

Figure 2 is a curve developed by use of a standard solution of sodium sulfate, the readings being confirmed by a number of individuals. It should be remembered, however, that eyes vary, and especially so where the eye is focused on an object, as in this case, instead of observing the intensity of light on a given area. A person using glasses, therefore, will expect to obtain readings different from those obtained by one not using glasses. The variations, however, are uniform over the curve and the variation may be used as a constant or a new curve may be drawn to meet the specific conditions.

In Table II are given parallel determinations by use of the turbidimeter, as compared with the results by the ordinary gravimetric process. These results were also obtained on boiler waters with widely varying amounts of caustic and sodium carbonate.

Table II—Turbidimeter Results for Sulfates in Boiler Water

Water No.	Turbidimetric	Gravimetric
	P. p. m.	*P. p. m.*
17206	1770	1742
17299	1550	1582
17300	1482	1499
17318	808	812

It is believed that the sharpness of the end point and the good agreement obtainable by this instrument will make it of practical utility, especially in the power plant.

Application of a Bromine Method in Determination of Phenol and Cresols[1]

R. D. Scott

Ohio Department of Health, Columbus, Ohio

With the increasing application of dephenolizing treatments to coke oven gas condensates in order that water supplies may not be contaminated by phenolic compounds, there is need for accuracy of method in determining the phenols content of the wastes before and after treatment.

While a method based on the combination of phenols with iodine has been considered more accurate than various bromine methods, data are presented which show that under certain prescribed conditions a bromine method yields the more accurate results.

Within the last five years dephenolization of those coke oven liquors which eventually reach public water supply intakes, in order to eliminate so far as may be practicable the development of objectionable tastes following chlorination, has become a general practice.

To measure the efficiency of dephenolizing plants, the need exists for an accurate method of determining the phenols content of these wastes before and after dephenolization; the work to be described was prompted by the belief that existing methods are not sufficiently accurate.

The Skirrow (*12*) procedure for the estimation of phenols in gas liquors, the Rose and Sperr (*10*) modification of which is at present in general use, may be separated into two parts, first the removal of interfering substances, and second the combination of phenol and cresols with iodine, employing the method of Messenger and Vortmann (*7*). The procedure is subject to material errors, both in the removal of interfering substances and in the final determination of phenols. In this paper, only the determination of phenols is considered, preliminary purification being assumed.

Several bromine methods are also in use. For instance, U. S. Steel Corporation chemists (*14*) add bromine in excess, acidify, then dry and weigh the precipitate of bromine compounds of phenol and cresols. Williams (*13*) applies a bromine titration after preliminary purification. Shaw (*11*) has developed a method using a specialized preliminary distillation followed by a determination of the phenols in the distillate turbidimetrically with bromine.

[1] Received August 5, 1930.

Iodine Methods

Theoretically, phenol and *m*-cresol form triiodo compounds, while *o*-cresol and *p*-cresol form diiodo compounds. In the application of the Messenger-Vortmann method to mixtures all are conventionally calculated to phenol, C_6H_5OH, as triiodo compounds, according to the reaction:

$$C_6H_5OH + 6I + 3NaOH = C_6H_2I_3OH + 3NaI + 3H_2O$$

Thus, theoretically only two thirds of the *o*- and *p*-cresols present would be reported. Actually with these two cresols the proportion of iodine fixed is more than the requirement for the diiodo compounds and less than the requirement for the triiodo compounds.

The writer found that with *o*-cresol the iodine fixed was 118.8 per cent and with *p*-cresol 137.0 per cent of theory for the diiodo compound. Thus, only 79.2 per cent of the *o*-cresol and 91.3 per cent of the *p*-cresol present in a mixture would have been reported, applying the triiodo calculation.

Redman, Weith, and Brock (*9*) modified the Messenger-Vortmann method by substituting sodium bicarbonate for sodium hydrate and obtained results near to theory when working with phenol and the separate cresols. The writer, employing their method, also obtained results near to theory, phenol and *m*-cresol being calculated as triiodo compounds and *o*-cresol and *p*-cresol as diiodo compounds.

However, while this modification yields more accurate results than the Messenger-Vortmann method as employed by Skirrow, there still exists the error due to the unknown and no doubt varying proportions of phenol and the indi-

vidual cresols present, when the method is applied to waste liquors.

It was also incidentally observed by the writer that the proportion of alkali recommended by Skirrow, 4 mols sodium hydroxide to 1 mol phenols (Messenger and Vortmann advised the use of at least 3 mols), does not yield maximum results for mixtures of phenol and cresols. It was found that higher results for *o*- and *p*-cresols, which were nearer to theory for the formation of triiodo compounds, were obtained by taking 6 mols of sodium hydroxide to 1 mol of cresol.

Bromine Methods

Koppeschaar (*5*) appears to have first applied bromine to the quantitative determination of phenol, using bromine water but later substituting a mixture of potassium and sodium bromides and bromates. He considered that the method was equally suitable for phenol or cresols, but was unable to investigate this point since he lacked pure cresols. In the bromide-bromate solution he used the equivalent of 2 grams of potassium bromate and 7.1 grams of potassium bromide per liter. (The present U. S. Pharmacopeia method for the assay of phenol calls for 3 grams of potassium bromate and 50 grams of potassium bromide per liter.) One hundred cubic centimeters of this solution were allowed to act on 0.1 gram of phenol for 15 minutes, then 10 cc. of potassium iodide, 125 grams per liter, and 5 cc. of concentrated hydrochloric acid solution were added.

Ditz and Cedivoda (*3*) noted that *o*- and *p*-cresols yield results differing from phenol and *m*-cresol, tending to form dibromo compounds in contrast to the tribromo compounds formed by phenol and *m*-cresol; they concluded also that while tribromophenol brom is completely reduced to tribromophenol by hydriodic acid, dibromo-*p*-cresol brom is only partially reduced; further that in the presence of a large excess of bromine *o*- and *p*-cresols may form tribromocresol broms.

Autenrieth and Beuttel (*1*) found that if bromine is added to *p*-cresol in only slight excess the precipitate is a mixture of dibromocresol brom and dibromocresol. With a large excess of bromine reacting for several days the precipitate was largely (about 88 per cent) converted into tribromophenol brom.

Lloyd (*6*) in a study of the bromine determination of phenol only, concluded that irregularities in results are due to the formation of varying amounts of tribromophenol brom and that this compound is not quantitatively converted into tribromophenol by hydriodic acid. He noted that the formation of tribromophenol brom was promoted by the presence of large excess of bromine and prolonged reaction, while its formation was repressed by the presence of a considerable concentration of acid and also of potassium bromide.

Pence (*8*) investigated a number of the factors affecting the bromine estimation of phenol and cresols. He found that prolonged reaction with a considerable excess of bromine gave higher results for *o*- and *p*-cresol than could be accounted for by the formation of either di- or tribromocresol broms and that reduction with potassium iodide was incomplete, higher results being obtained for *o*-cresol than for *p*-cresol. With *m*-cresol results were nearer theory for the formation of tribromocresol brom, followed by complete reduction to tribromocresol by potassium iodide, but high results were noted on prolonged standing with bromine.

Redman, Weith, and Brock (*9*) confirm the results of Pence and conclude that *o*- and *p*-cresol broms are not readily reduced by potassium iodide because the precipitate of these compounds condenses into dense particles which do not afford free access to the hydriodic acid. They state that with the bromine method the results are too dependent upon the dexterity and patience of the individual experimenters.

Kolthoff and Furman (*4*) conclude that phenol and *m*-cresol are accurately determined with bromine, while *o*- and *p*-cresol require somewhat more than two bromine atoms, the quantity of bromine taken up being dependent upon the amount in excess, the acid concentration, and the time of reaction.

Thus it appears that various reactions may take place upon the bromination of cresols and their subsequent reduction with hydriodic acid, and that their determination by the use of bromine has not met with much favor.

However, preliminary studies led the writer to the opinion that for the purpose of determining phenol and cresols in mixtures, such as for example, gas liquors and coke oven wastes, bromination offered possibilities of greater accuracy than the present iodine methods, and as a result of further experimental work a method was devised with which satisfactorily accurate results may be obtained.

In this work, the data of which is too extensive to be shown in full, the phenol used was a C. P. grade further purified by distillation, retaining the middle third. The cresols used were the "practical" grade of the Eastman Kodak Company, purified by distillation, retaining the middle third, redistilling this portion, and finally retaining the middle third. Some comparisons were also made with Kahlbaum's cresols, redistilling and retaining the middle third; no material differences were noted.

Experimental Data

Concentration of Acid—Increase in concentration of hydrochloric acid in the range from 0.05 *N* to 0.25 *N* yielded progressively higher results for *o*- and *p*-cresol, *o*-cresol being the more affected. With higher concentrations the results were not materially higher and some liberation of iodine occurred by the acid alone acting upon potassium iodide. With phenol and *m*-cresol low results were noted with 0.05 *N* acid, maximum results with 0.1 *N*, the same results with 0.25 *N*, and low results with 1.25 *N*.

Concentration of Potassium Iodide—Increase in concentration of potassium iodide in the range from 0.01 to 0.20 molar yielded progressively lower values for *o*-cresol. With *p*-cresol, *m*-cresol, and phenol no material differences were noted.

Duration of Reduction with Potassium Iodide—Increase in the time allowed for reduction with potassium iodide in the range from 2 minutes to 2 hours yielded progressively materially lower results for *o*-cresol. With *p*-cresol, *m*-cresol, and phenol only a slight progressive decrease in results was noted.

Duration of Bromination—Increasing the time allowed for the reaction with bromine in the range from 5 minutes to 4 hours yielded progressively much higher results for *o*- and *m*-cresol. A smaller progressive increase was noted for *p*-cresol and a still smaller increase for phenol.

Excess of Bromine—Raising the excess of bromine present, either by adding more potassium bromate or by taking smaller amounts of phenols, yielded progressively much higher results for *o*-cresol. With *p*-cresol, *m*-cresol, and phenol a much smaller increase in results was noted.

Temperature during Bromination—Increase of temperature in the bromine reaction in the range from 20° to 30° C. yielded materially higher results for *o*-cresol and *p*-cresol. With *m*-cresol and phenol no material change in results was noted.

Volume of Solution—Increase in volume of the solution containing phenols, in the range 25 to 250 cc., yielded progressively higher results for *o*- and *p*-cresols. With *m*-cresol a smaller increase was noted and with phenol a still smaller increase. Increase in volume to 700 cc. yielded

much lower results in each case. It was observed that with a solution containing 0.025 gram of phenol or cresol in 200 cc., bromination produced a large volume of precipitate with phenol, a smaller amount with *m*-cresol, a very scanty precipitate with *p*-cresol, and no precipitate with *o*-cresol.

Concentration of Potassium Bromide—Increase in concentration of potassium bromide in the range 0.03 to 0.31 molar yielded a large progressive decrease in results for *o*-cresol, while with *p*-cresol a small progressive increase in results was noted. With *m*-cresol and phenol a small progressive decrease in results was noted. The results of variation in potassium bromide concentration are shown in Table I.

Table I—Effect of Potassium Bromide Concentration

Phenol or cresol taken, 0.0250 gram
Solution containing phenol or cresol, 200 cc.
$KBrO_3$ added, 25 cc. solution containing 3 grams in 1 liter
Acid added, 10 cc. 1:1 HCl
KBr added, 25 cc. solution containing 200 grams in 1 liter
Duration of bromine reaction, 1 hour; temperature, 25° C.
Duration of KI reduction, 30 minutes
$Na_2S_2O_3$, 0.9830 0.1 *N*; 25 cc. = 27.22 cc. $KBrO_3$ solution

KBr	Phenol		*o*-Cresol		*m*-Cresol		*p*-Cresol	
	$Na_2S_2O_3$	Wt. Phenol	$Na_2S_2O_3$	Wt. *o*-Cresol	$Na_2S_2O_3$	Wt. *m*-Cresol	$Na_2S_2O_3$	Wt. *p*-Cresol
Grams	*Cc.*	*Gram*	*Cc.*	*Gram*	*Cc.*	*Gram*	*Cc.*	*Gram*
0.75	16.52	0.02543	15.72	0.02780	14.52	0.02568	13.97	0.02470
1.50	16.32	0.02512	15.44	0.02730	14.42	0.02550	14.00	0.02475
3.00	16.24	0.02500	15.04	0.02659	14.12	0.02497	14.07	0.02488
6.25	16.22	0.02497	14.12	0.02497	14.02	0.02479	14.10	0.02493
10.00	16.20	0.02494	12.92	0.02285	13.92	0.02462	14.17	0.02506

In general, the results for phenol and *m*-cresol are not greatly affected by changes in the factors noted. *o*- and *p*-cresol are in general affected to a greater extent, *o*-cresol the more markedly with a tendency toward high results, *p*-cresol with a tendency toward low results. Thus, the problem is largely the adaptation of the various factors involved in the direction that lower results would be obtained for *o*-cresol and higher results for *p*-cresol.

Bromine Method for Phenol and Cresols

It was found possible to take advantage of the data obtained in this experimental work to devise a method which has been found to yield reasonably accurate results for phenol as well as for *m*-, *o*-, and *p*-cresol, singly or in mixture, as follows:

After carrying the sample through a suitable preliminary purification treatment, take an aliquot estimated to contain about 0.02 gram of phenol or cresols in terms of phenol and transfer to a 500-cc. glass stoppered flask. Add just enough distilled water to make the volume 200 cc. Add 25 cc. (measured) of potassium bromide solution containing 250 grams in one liter. Add 10 cc. of 1:1 hydrochloric acid solution and place in a water bath held at 25° C. Let stand until the temperature of the solution is 25° C. Add exactly 25 cc. of potassium bromate solution containing 3 grams in one liter. Mix well, then let stand at 25° C. (preferably within 1 degree, at most within 2 degrees) for exactly 60 minutes, shaking two or three times during this period. At the end of this time add 25 cc. of potassium iodide solution containing 200 grams in one liter, mix well, and let stand at 25° C. for exactly 30 minutes, shaking two or three times during this period.

Titrate the liberated iodine with 0.1 *N* sodium thiosulfate, adding starch solution near the end of the titration and disregarding any return of the blue starch-iodine color. Run a blank determination in the same manner.

The difference between the two titrations times 0.0015675 equals the weight of phenol and cresols in terms of phenol. The calculation is made according to the empirical reactions for cresols:

$$C_6H_4.CH_3OH + 8Br = C_6H.CH_3Br_3OBr + 4HBr \quad (1)$$
$$C_6H.CH_3Br_3OBr + 2HCl + 2KI = C_6H.CH_3Br_3OH + 2KCl + I_2 + HBr \quad (2)$$

The net result is 6 mols of bromine for 1 mol of cresol, a similar reaction taking place with phenol. While these reactions may go to practical completion with *m*-cresol, with *o*- and *p*-cresol it is probable that the first reaction only partially takes place, further that the tribromocresol broms which may be formed are incompletely reduced by hydriodic acid to tribromocresols, in which event high values would result. It is probable also that there is a considerable formation of dibromocresol broms with incomplete reduction to dibromocresols, with resulting low values when calculated as tri- compounds, and in addition there may be some conversion of tribromocresols into tribromophenol.

Table II—Results with Various Weights of Phenols

Weights Taken	Weights Found				
	Pheuol	*o*-Cresol	*m*-Cresol	*p*-Cresol	Composite
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0400	0.03947	0.03627	0.03947	0.03867	0.03816
0.03500	0.03463	0.03306	0.03459	0.03425	0.03420
0.03000	0.02980	0.02915	0.02972	0.02951	0.02984
0.02500	0.02496	0.02504	0.02482	0.02490	0.02492
0.02000	0.02000	0.02057	0.01986	0.02000	0.02010
0.01500	0.01500	0.01596	0.01494	0.01504	0.01514
0.01000	0.01006	0 01084	0.01000	0.09980	0.01008
0.00500	0.00504	0.00579	0.00495	0.00499	0.00518

Table III—Effect of Temperature

Temp. of Soln.	Weights Found				
	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol	Composite
° *C.*	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
20	0.02489	0.02417	0.02460	0.02426	0.02452
23					0.02473
25	0.02489	0.02492	0.02469	0.02487	0.02496
27					0.02509
30	0.02489	0.02584	0.02489	0.02540	0.02523

The method presented would seem to provide a balance of these conditions which yields nearly theoretical results.

The above method is accurate for phenol, *o*-, *m*-, and *p*-cresol when the weight present is about 0.022 gram. In the case of phenol, *m*-, and *p*-cresol, considerable variation from this weight does not materially affect the accuracy of the determination. However, with *o*-cresol extreme variations from this weight do materially affect the accuracy of the method. Thus, taking 0.022 gram of *o*-cresol, 100.16 per cent of theory was found; with 0.0261 gram, 97.17 per cent; with 0.0174 gram, 102.85 per cent.

With wastes such as gas liquors and coke oven wastes, while the proportion of *o*-cresol is uncertain and variable, it probably does not exceed one fourth of the total weight of phenol and cresols. On this basis, no appreciable error will be introduced if the indicated weight of phenols in terms of phenol is from 0.01 to 0.03 gram, equivalent to from 6.4 to 19.1 cc. of 0.1 *N* bromine fixed.

If the indicated amount of phenols is without this range, the determination should be repeated, using an aliquot which will fall within these limits.

If the concentration of phenols in the sample examined is so low that it is not practicable to have as much as 0.01 gram present in a volume of 200 cc., it is still possible to obtain results of considerable accuracy by increasing the concentration of potassium bromide. Thus, for weights of phenols of from 0.005 to 0.1 gram, 55 cc. of potassium bromide solution should be added.

Results noted with the method are shown in Table II, 1 cc. of 0.1 *N* bromine being calculated as equivalent to 0.0015675 gram phenol and 0.001801 gram cresol. The results under the heading "Composite" were obtained with

a mixture of 4 parts of phenol, 2 parts of *o*-cresol, 1 part of *m*-cresol, and 1 part of *p*-cresol.

The effect of variation in temperature is shown in Table III, the weight taken in each case being 0.025 gram. There remains the error due to calculation of both cresols and phenol in terms of phenol. This may be eliminated if desired, by applying the method of Chapin (*2*) to estimate the proportion of phenol present in the mixture of phenol and cresols.

Literature Cited

(1) Autenrieth and Beuttel, *Arch. Pharm.*, **248**, 112 (1910).
(2) Chapin, U. S. Dept. Agr., *Bull.* **1308**, 17 (1924).
(3) Ditz and Cedivoda, *Z. anal. Chem.*, **38**, 873 (1899).
(4) Kolthoff and Furman, "Practical Volumetric Analysis," Vol. II, p. 475, Wiley, 1929.
(5) Koppeschaar, *Z. anal. Chem.*, **15**, 233 (1876).
(6) Lloyd, *J. Am. Chem. Soc.*, **27**, 7 (1905).
(7) Messenger and Vortmann, *Ber.*, **23**, 2753 (1890).
(8) Pence, J. Ind. Eng. Chem., **4**, 518 (1912).
(9) Redman, Weith, and Brock, *Ibid.*, **5**, 831 (1913).
(10) Rose and Sperr, *Am. Gas Assocn. Monthly*, **2**, 117 (1920).
(11) Shaw, Ind. Eng. Chem., Anal Ed., **1**, 118 (1929).
(12) Skirrow, *J. Soc. Chem. Ind.*, **27** (2), 58 (1908).
(13) Williams, Ind. Eng. Chem., **19**, 530 (1927).
(14) U. S. Steel Corporation, "Sampling and Analysis of Coal, Coke, and By-Products," p. 153, Carnegie Steel Co., 1929.

Should a Change Be Made in Analytical Procedure for Evaluating Available Phosphoric Acid Content of Fertilizer Materials?[1]

C. C. Howes and C. B. Jacobs

Davison Chemical Co., Baltimore, Md.

THE rapidly changing fertilizer industry demands that a constant watch be kept on the methods of analysis used to evaluate the plant food content of materials offered.

Most of our present methods have been in use for many years. From time to time minor changes have been made in order that they will be suitable for a greater variety of work.

The present method of determining the available phosphoric acid has recently come into a prominent position due to the introduction of synthetic ammonia as a potential nitrogen-bearing fertilizer material. The use of ammonia either in the anhydrous or aqua form is dependent chiefly on the amount of this material that can be chemically combined with the superphosphate to which it is added. During recent experiments to study conditions accompanying the injection of ammonia into superphosphate, a number of difficulties were encountered with the present official method for determining the insoluble P_2O_5.

Table I—Insoluble P_2O_5 in Ammoniated Superphosphate
Ammonia content, 3.50 to 6.00%

Insoluble P_2O_5		Insoluble P_2O_5	
2-gram sample	1-gram sample	2-gram sample	1-gram sample
%	%	%	%
4.67	2.30	2.46	0.44
0.94	0.33	2.12	1.08
1.78	0.60	3.08	1.36
1.16	0.60	5.09	3.20
1.02	0.32	3.97	1.78
0.86	0.22	1.42	0.46
0.98	0.32	1.72	0.62
3.42	1.68		
3.84	1.60		

This method has been in use with little change for many years and it was with hesitancy, even after thorough painstaking analyses, that these variations were reported. The first of these irregularities was observed when we departed from the official procedure by using a 1-gram portion instead of 2. This deviation was made because it was at first thought that on the addition of ammonia too much dicalcium phosphate had been formed to be soluble in the 100 cc. of neutral ammonium citrate solution. With this deviation the insoluble P_2O_5 present was changed entirely as will be noted in Table I.

Table II—Effect on Insoluble P_2O_5 Results by Varying pH Value of Ammonium Citrate Solution

Ammonium Citrate Soln.	Insoluble P_2O_5	
	Ammoniated superphosphate	Superphosphate (not ammoniated)
pH	%	%
4.5	0.97	0.62
5.0	0.98	0.62
5.2	1.00	0.60
5.3	0.98	0.63
5.4	1.06	0.62
5.6	1.16	0.60
5.8	1.26	0.61
6.0	1.54	0.62
6.3	2.94	0.62
6.6	4.23	0.63
7.0	4.67	0.61
7.8	6.34	0.62
8.4	8.12	0.69
8.8	8.60	0.71
	with 1-gram portion	
7.0	2.30	0.60

After making a number of insoluble determinations on different samples containing varying amounts of ammonia, it became necessary to make up a new neutral ammonium citrate solution. The citrate solution was made up following the prescribed official procedure, using phenol red as the indicator. Following the preparation of the new batch of citrate solution several samples were run that had previously been run with the old citrate solution. The results of these differed very widely from those obtained with the old solution. With these variations it was believed that the difficulty lay in the citrate solution. Upon determining the true reaction of the first citrate solution it was found to have a pH value of 6.5, while the new citrate solution prepared last had a pH value of 7.0. This led to the belief that a slight variation in the pH value of the citrate solution may cause wide variations in the insoluble P_2O_5 results, in material to which ammonia has been added. A number of citrate solutions were then made up with pH values ranging from 4.5 to 8.8. Samples to which ammonia had been added to the extent of 5.76 per cent were then analyzed with

[1] Received September 22, 1930. Presented as a part of the Symposium on "Action of Ammonium Citrate on Superphosphates," before the Division of Fertilizer Chemistry at the 80th Meeeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

each of these citrate solutions. Table II shows the results of this experiment. In addition to these figures a 1-gram portion was analyzed with the citrate solution having a pH value of 7.0. An insoluble P_2O_5 figure of 2.3 was obtained, while it will be noted that the 2-gram portion gave an insoluble P_2O_5 of 4.67 per cent. An experiment similar to that shown in the previous tabulation was made with a normal superphosphate—that is, one to which no ammonia had been added. The results of this experiment are also shown in this table.

It will be noted that the variations obtained with the normal superphosphate are within the limits of experimental error.

Another experiment to study the effect of varying the ratio of sample to citrate solution was then carried out, in a 65° C. bath for 30 minutes, on a 2-gram sample of normal superphosphate and on one which had been ammoniated 6.2 per cent. An ammonium citrate solution having a pH value of 7.0 was used. Table III gives the results of this experiment.

Table III—Effect on Insoluble P_2O_5 Results by Varying Amount of Citrate Solution

Superphosphate	Ammonium Citrate					
	100 cc.	200 cc.	250 cc.	300 cc.	350 cc.	400 cc.
	%	%	%	%	%	%
Not ammoniated	0.83	0.78	0.74	0.69	0.66	0.64
	1.90	1.82	1.80	1.82	1.76	1.76
Ammoniated	5.46	2.54	2.01	1.64	1.80	1.49

It will be noted from these results that extreme variations are obtained with ammoniated goods, while the variations with a normal superphosphate are much less and scarcely more than that due to experimental error.

Another series of analyses was made to study the effect of the time of exposure of sample to citrate solution, on both the normal superphosphate and ammoniated superphosphate. In this series both a 1-gram portion and a 2-gram portion of sample were used. These results are shown in Table IV.

Table IV—Effect on Insoluble P_2O_5 Results by Varying Periods of Digestion

Superphosphate	2-Gram Sample			1-Gram Sample		
	1/2 hr.	1 hr.	1 1/2 hrs.	1/2 hr.	1 hr.	1 1/2 hrs.
	%	%	%	%	%	%
Not ammoniated	0.83	0.59	0.59	0.74	0.60	0.58
	1.90	1.74	1.74	1.84	1.80	1.76
Ammoniated	5.46	4.33	4.32	1.64	0.78	0.68

Difficulties with Official Method

The official method as it now stands seems to serve well in cases where ammonia has not been introduced, but from the data given in the preceding tabulations it is quite evident that this method will not serve without alteration in cases where ammonia has been introduced. Under the present status innumerable difficulties may be expected. For instance, let us picture for a moment conditions where a manufacturing department depends entirely on the laboratory to govern the compounding of its materials. Good practice demands that the laboratory follow the official method as closely as possible. Let us suppose that ammoniated superphosphate is to be used to compose a mixture. The analyst is required to weigh a 2-gram portion. The results of his analysis will be used to calculate the desired amount of the ammoniated superphosphate to be used. Let us suppose further that in compounding this mixture a 16 per cent available P_2O_5 will be used to give an 8 per cent available P_2O_5 in the finished product. When the sample of the finished material is submitted to the laboratory a 2-gram portion is again weighed. This means that there is the equivalent of only 1 gram of the ammoniated superphosphate taken in the analysis. Let us for a moment refer back to Table I and the first illustration given. This sample shows, with a 2-gram portion, 4.67 per cent insoluble P_2O_5, and with a 1-gram portion, 2.30 per cent insoluble P_2O_5, a difference of 2.37 per cent insoluble phosphoric acid. Such practice could not be tolerated very long. It would mean either reworking the material or sustaining a loss of 2.37 units of phosphoric acid. The same results in varying degrees will be found, depending upon the amount of ammoniated superphosphate used to compose the finished fertilizer mixture.

In addition to plant control difficulties, an unfair discrimination is made against the manufacturer of ammoniated superphosphate in favor of the dry mixer who uses it. The present official method specifies that the ammonium citrate solution shall be neutral, but further states that phenol red may be used as the indicator to determine the neutral point. This leaves it optional with the analyst where no standard indicator solutions are available, as to what the neutral point with phenol red may be. His choice of the neutral point may be anywhere between 6.8 and 8.4, although one would not expect extreme variations. As a matter of curiosity, samples of supposedly neutral ammonium citrate were obtained from a number of laboratories engaged in fertilizer work. The pH value was determined on each of these solutions and they were found to have a range from 6.1 to 7.1. Referring back to the insoluble determinations shown in Table II and visualizing material of this nature being compounded according to the results yielded with the citrate solution having a pH value of 6.1 and later being analyzed in a state control laboratory with a citrate solution having a pH value of 7.0, the results would have a great tendency to place the manufacturer offering such goods in a very bad position. Should it so happen that the pH value of the citrate solutions of the plant control laboratory and the state laboratory be reversed, the results would have a tendency to cause the factory management to make a change in their personnel. However, the results obtained with citrate solutions covering the pH range just mentioned, applied to unammoniated goods, would be satisfactory as shown in Table V.

Table V—Variations in Insoluble P_2O_5 Results with Change in pH Value of Citrate Solution

Weight of Sample	Citrate-Insoluble P_2O_5 When pH of Citrate Solution Is:										NH_3
	7.0	6.7	6.5	6.2	5.7	5.4	5.0	4.6	4.2	3.5	
Grams	%	%	%	%	%	%	%	%	%	%	
Normal superphosphate—slight variation											
2	0.19	0.18	0.16	0.16	0.17	0.16	0.17	0.16	0.16	0.16	None
1	0.18	0.18	0.18	0.17	0.16	0.20	0.17	0.18	0.16	0.16	
2	2.10	2.10	2.11	2.10	2.06	2.11	2.14	2.15	2.24	2.16	None
1	2.04	2.18	2.14	2.08	2.10	2.16	2.14	2.14	2.22	2.12	
Ammoniated superphosphate—wide variation											
2	6.66	6.49	6.19	4.52	3.09	2.64	1.89	1.77	1.29	0.72	5.78
1	4.12	4.12	3.60	1.62	0.84	0.66	0.58	0.58	0.56	0.44	
2	5.80	5.80	5.65	3.11	1.84	1.32	0.97	0.80	0.57	0.50	5.03
1	2.54	2.44	2.14	0.62	0.48	0.46	0.46	0.44	0.46	0.42	
2	6.36	6.20	6.12	4.65	3.33	2.76	2.50	2.03	1.41	0.87	5.76
1	4.24	4.26	3.80	2.00	1.16	0.72	0.56	0.58	0.52	0.40	
2	6.46	6.37	6.31	4.59	3.36	2.63	2.18	1.66	1.35	0.64	4.76
1	3.76	3.68	3.44	1.72	0.92	0.70	0.66	0.62	0.62	0.48	
2	5.32	5.26	4.98	3.54	2.07	1.35	1.00	0.66	0.48	0.25	6.21
1	3.48	3.34	3.20	0.98	0.38	0.32	0.30	0.32	0.27	0.26	

New Method Advocated

The main points at issue are: First, that the official method for the determination of insoluble P_2O_5 as it now stands is applicable in cases where ammonia has not been introduced,

and the least that can be done is to pay a tribute to the authors who have contributed to such a method that has served well for so many years. We are now confronted with rapidly changing practices and materials, and it is very obvious that it may become necessary to devise an entirely new method to take care of this new product. By continuing with the present method, a hardship is being worked on the manufacturers of fertilizers and on the manufacturers of synthetic and by-product ammonia, as well as on the users of fertilizers. There is no doubt but that the injection of ammonia into fertilizer materials will remedy a number of difficulties with which the manufacturer and farmer have contended for a number of years. By this statement a reduction in the free acid content and an improvement in the storing and drilling qualities of fertilizer materials is meant.

By an injection of ammonia as such into superphosphate or superphosphate-bearing fertilizer materials, it is only with the greatest difficulty that the so-called reversion of the available phosphate is prevented. Numerous publications by various investigators lead to the belief that most of the available phosphoric acid under its present classification reverts to an insoluble form shortly after application to the soil. A number of investigators have also shown that phosphoric acid in that condition is still available as plant food. If these reports be true, and there is every reason to believe that they are, then it seems only reasonable and fair to both the manufacturer and the user that a thorough study be made as promptly as possible of the compounds formed in superphosphate during the injection of ammonia, with a view towards reclassifying and reinterpreting the term "available." Such an investigation involves a large number of pot and field tests and would necessarily have to be accompanied by a large amount of laboratory work. The writers understand that much of this work is now under way.

This seems to be one of the most important manufacturing problems with which the fertilizer industry is confronted today. Much benefit will result to all concerned if the maximum amount of this form of nitrogen can be used. It is essential that this question be very definitely worked out and as soon as possible, because the manufacturer must necessarily anticipate his processes of the future.

It is a duty of this organization to lay aside all precedent and carry on a well organized system of experiments, the results of which will answer the questions with which we are confronted.

Measurement of Abrasion Resistance

I—Paints, Varnishes, and Lacquers[1]

A. E. Schuh and E. W. Kern

Bell Telephone Laboratories, 463 West St., New York, N. Y.

A method of measuring the abrasion resistance of materials in the form of thin films has been devised. While designed primarily for the study of paint, lacquer, and varnish films, the method should be useful also in the study of a wide range of other materials. The method consists essentially in the following: Carborundum powder of uniform particle size is admitted at a constant rate to a directed stream of air under constant pressure and the resulting Carborundum-air blast is allowed to impinge upon a film of the test material mounted at a fixed angle. The weight of Carborundum required to wear through a unit thickness of material is taken as the abrasion resistance of the material. The development of this test has included an investigation of the variables pertaining both to the apparatus and to the material under test.

SINCE organic finishes such as paints and varnishes are often subject to abrading forces, it is desirable to evaluate them with respect to their resistance to abrasion. Several methods have been developed for this purpose, some of which have been described by Gardner (*1*). Among these, the Parlin method is representative of a type of test in which an abrading surface is moved at controlled pressure and speed over the organic film, and the abrasion value taken as the number of passes required to cut through the material. This method is open to criticism in that an appreciable frictional heating is produced at the interface of film and abrasive and, furthermore, that the abrading surface undergoes variation with use. On the other hand, Gardner's falling sand method, in which the abrasive falls by gravity through a long confining tube and impinges on the paint film, appeared more suitable in principle for the development of a precise test. The method to be described in the present paper has employed a modification of this principle in that air at carefully controlled pressure is used to drive the abrasive against the film under test.

The present abrasion test consists essentially in admitting a stream of Carborundum particles into a rapidly flowing air stream and allowing the uniform mixture of air and Carborundum to impinge against a film of known thickness of the material to be tested. The weight of Carborundum required to wear through the film is measured and arbitrarily defined as the abrasion value for a given thickness of the material. Obviously, in order to obtain reproducibility of measurement, it becomes necessary to hold the conditions of the test constant. With a view to making the method generally applicable, the variables that affect the abrasion value have been studied both as to their nature and relative magnitude.

Although the method is by no means restricted to the determination of relative abrasion resistance of paint films, the test has been developed using these as the test materials. It is well known that the properties of material of this type, especially when of oleoresinous origin, are much affected by temperature and humidity. It seemed necessary, therefore, to carry on this study under controlled air conditions. The effect of temperature and humidity of the air was investigated over a wide range of indoor variation, the air conditions ranging from 21.1° C. (70° F.) and 41 per cent relative humidity to 32.2° C. (90° F.) and 90 per cent relative humidity. The materials tested were: (1) three varnishes of differing oil lengths but of a common synthetic resin; (2) two series of lacquers each of a different resin in three different concen-

[1] Received September 19, 1930. Presented before the Division of Paint and Varnish Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

trations; (3) a baked japan, a baked varnish, and a varnish enamel.

Apparatus and Procedure

The abrasion machine, which is shown together with pressure regulating devices in Figure 4, consists essentially of a box into the upper portion of which a nozzle confining the air-Carborundum stream is inserted. An adjustable table, upon which the sample to be tested is mounted, is brought into position against the lower end of the nozzle. For films over opaque base materials, illumination is effected from the front through a window in a door through which the sample is introduced. For films over transparent base, illumination is effected through a window in the rear. The Carborundum falls into a lower compartment of the box and a finely meshed screen allows the air to escape while retaining the Carborundum. For an actual determination, the test specimen is mounted in place, the air turned on, and when at equilibrium pressure, the Carborundum stream is started by removing a pinch clamp from the tube leading to the weighed container of Carborundum situated above the abrasion box. As soon as the blast of abrasive wears through the film revealing the underlying base uniformly over a small area about 2 mm. in diameter, the Carborundum stream is shut off and the loss in weight of the Carborundum container measured. The thickness of the film is determined at several points at the edge of the wear spot and the number of grams required to wear through unit film thickness calculated.

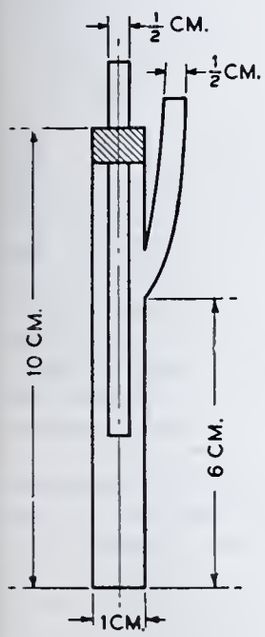


Figure 1—Diagram of Nozzle

In the present study, air at the desired temperature and humidity was obtained by compressing the air from the room, which was automatically conditioned. The heat generated by compression was dissipated by allowing the air to flow through a copper coil within a large water bath held at room temperature. The pressure of the air was then regulated by an adjustable T-outlet in a column of water. An equalizing reservoir was employed to smooth out minute fluctuations. Pressure as delivered to the abrasion machine was determined by means of a mercury manometer.

The heart of the instrument consists of the nozzle in which the air and Carborundum streams are intimately mixed. Many designs were tried and for the present development a nozzle shown in Figure 1 was employed.

This design combines simplicity of construction with ease of duplication, and it has made possible measurements of high precision. For ease of duplication of nozzles, a straight air tube was found essential, since any bends or kinks markedly affected the abrasion value obtained. In order to calibrate a new nozzle of this same design against a nozzle of known performance, it was necessary only to adjust the position of the inner air tube, by lowering or raising, with respect to the outer confining tube. The difference of diameters of the two tubes produces a flaring of the air stream with the result that the Carborundum which is introduced by gravity at any suitable point above the end of the inner tube is uniformly mixed with the air.

Variables Pertaining to Method

Since this study was conducted on paint films of various types, which unfortunately are variable in both physical and chemical behavior, it seemed desirable to segregate the variables that pertain to the method from those dependent on the material tested. Consequently, the various test variables are first discussed, and afterward the application of a standardized test to a variety of materials is shown.

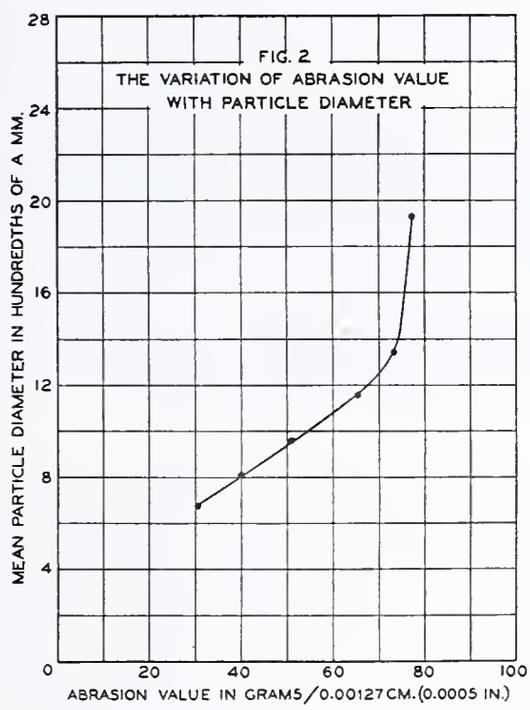
Effect of Position of Test Specimen on Abrasion Value—The position of the test specimen with respect to the end of the nozzle was varied both in distance from the end and in angle with respect to nozzle. The results are summarized in Table I.

Table I—Effect of Position of Test Material, Lacquer No. 18, on Abrasion Value

Distance from Nozzle	Angle to Perpendicular	Abrasion Value
Cm.	*Degrees*	*Grams*
0.0	45	31.8
0.5	45	35.8
1.0	45	44.5
0.0	30	22.2
0.0	45	31.5
0.0	60	50.1

The selection of a definite position is more or less arbitrary, so that in all subsequent experiments the test specimen was placed against the nozzle and at 45 degrees.

Effect of Particle Size—By means of standard A. S. T. M. sieves of 80, 100, 120, 140, 170, 200, and 230 mesh Carborundum was separated in a mechanical shaker into the various intermediate fractions. Sufficient time was allowed in the shaker to permit reasonably clean separation. A lacquer film of known composition and thickness was then tested for abrasion resistance using these various fractions of Carborundum and keeping all other conditions of test constant.



The results of this experiment are given in Table II.

Table II—Effect of Particle Size on Abrasion Value

Mesh Size	Mean Diameter of Particles	Abrasion Value
	Cm.	*Grams/0.0127 mm.*
80–100	0.0193	77.5
100–120	0.0134	73.3
120–140	0.0115	65.2
140–170	0.0097	51.0
170–200	0.0081	40.0
200–230	0.0068	30.7

The variation of abrasion value with particle size is graphically shown in Figure 2. For the small particles, the relation seems to be linear. For practical purposes, a given range of

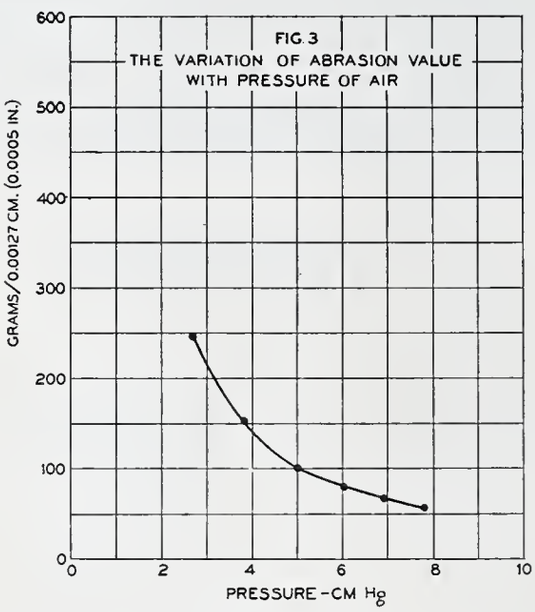
particle size must be selected, and since the smaller particles tend to give a more uniform wear spot the fraction between 170- to 200-mesh sieves was used in all succeeding experiments.

Effect of Air Pressure—In this experiment the effect of changes in air pressure alone was investigated. The results are given in Table III.

Table III—Effect of Air Pressure on Abrasion Value

Pressure	Abrasion Value
Cm. Hg	*Grams/0.0127 mm.*
2.8	246.5
3.85	151.8
5.0	99.6
6.0	79.0
6.9	66.9
7.8	56.5

Figure 3, graphically representing the values of Table III, shows how the abrasion value decreases as pressure increases. As higher pressures are approached, the rate of change of the abrasion value decreases. For this reason a pressure of about 6 cm. of mercury was selected as a standard condition. At this pressure the time required with the selected rate of flow of Carborundum was found convenient for all types of films tested.



Effect of Rate of Flow of Carborundum—The Carborundum from the container above the abrasion box passes through a small circular orifice, which by its size controls the rate of flow into the nozzle. A series of orifices was tested which gave a range of rate of flow of Carborundum from 12 grams per minute to 86 grams per minute. On holding all the other variables constant the abrasion value was found to drop from 86 grams at the slowest rate to 80 grams at the highest. In other words, a 700 per cent change in rate of Carborundum flow caused only an 8 per cent change in abrasion value, showing that the distribution of the Carborundum in the air stream is almost insensitive to its rate of introduction. A rate of flow of about 24 grams per minute of 170- to 200-mesh Carborundum was selected as standard.

Effect of Source and Use of Carborundum on Abrasion Value—Two separate lots of Carborundum were screened and the 170- to 200-mesh fraction was used to determine the abrasion value of a given material. The same average value was obtained in the two sets of determinations, the difference being within the experimental error.

Various experiments indicated that, if so desired, the same Carborundum could be used safely for several determinations. A 5-pound (2.3-kg.) lot of Carborundum of 170 to 200 mesh was used repeatedly in the course of 200 wear determinations. On comparison of this used Carborundum with fresh material the same abrasion values were obtained on a given film. Furthermore, a screen analysis of the used and unused Carborundum showed no reduction in particle size, although a microscopic examination at a magnification of 170 × revealed slight chipping on some of the cutting edges.

Reproducibility of Abrasion Value with Duplicate Nozzles—It is of practical importance to know how abrasion values on any one material can be duplicated with different nozzles of the same design. By using glass tubes of approximately equal bore, and adjusting the position of the inner tube, it was possible to construct a second nozzle which gave an average abrasion value for a given japan film of 100.4 grams as against 100.2 grams for the first nozzle.

For purposes of calibration of nozzles it was found desirable to use a test film of other than organic nature. A thin electroplated coat of cadmium or zinc over polished copper or brass proved satisfactory. It is well known that if the conditions of plating are held constant, a coating of uniform thickness is obtained. The exact amount of metal distributed over the surface is readily determined. In addition, the material is not subject to the physical and chemical variation which organic films show with age.

In recapitulation, the following conditions of operation were shown to be well adapted for the measurement of the abrasion resistance of paints, lacquers, and varnishes:

Position of test specimen—flush against end of nozzle and at 45-degree inclination
Particle size of Carborundum—170 to 200 mesh
Air pressure—6 cm. of mercury
Rate of flow of Carborundum—24 grams per minute

Application of Test

It now became of interest to apply this standardized test to the evaluation of the abrasion resistance of various organic finishing materials. For this study a number of different varnishes and lacquers were formulated. The varnishes designated as V-15, V-16, and V-17 were of the compositions shown in Table IV.

Table IV—Composition of Varnishes

Component	V-15	V-16	V-17
	% by wt.	*% by wt.*	*% by wt.*
Amberol resin	20.62	16.7	14.11
China wood oil	23.92	26.26	28.42
Linseed oil (bodied)	5.92	6.68	7.13
Lead acetate	0.15	0.165	0.18
Liquid cobalt	0.27	0.30	0.33
Mineral spirits	49.72	49.90	49.83
Total metal (ratio Pb:Co = 19:1)	0.086	0.095	0.103
Oil length, gal.	18	25	32

Six lacquers of the composition indicated in Table V were used.

Table V—Composition of Lacquers

Component	L-17	L-18	L-19	L-20	L-21	L-22
	%[a]	%	%	%	%	%
1/2-sec. cotton, dry basis	60.5	45.4	36.4	60.5	45.4	36.4
Ester gum	30.4	45.4	54.5	..	..	..
Amberol gum	..	..	..	30.4	45.4	54.5
Dibutyl phthalate	9.1	9.1	9.1	9.1	9.1	9.1

[a] All per cents by weight.

In addition to these materials, a baked varnish, a baked black japan, and a varnish enamel were studied. The abrasion values for these materials as given in the succeeding tables represent the mean of two or more readings with the precision of the order given in a later separate discussion on the precision of the method.

All of the test specimens were prepared on best grade window glass by the spinning disc method and the films were allowed to dry in a horizontal position. Glass was selected

as the base material because it is inert, relatively flat, and permits greater ease of observing end points. Furthermore, it was felt that the absolute abrasion value would be only slightly affected by this choice, since in the test, cohesion of the material primarily determines the values and adhesion plays only a small part. Only with extreme care was it possible to obtain thicknesses of good uniformity. In general, varnishes were better than the lacquers owing to their longer period of leveling. The uniformity of the lacquer films was definitely improved by the addition of slower evaporating solvents.

The thickness of the films was determined by means of an Ames dial gage reading to 0.0001 inch and permitting estimation of hundredths of a mil. The gage was checked against a Zeiss optimeter, Johannsen blocks, and a Pratt Whitney Super Micrometer, and showed excellent accuracy and precision. For use on compressible paint films, the practice of gently lowering the spindle of the gage on the surface was adhered to. An accuracy within ±0.02 mil was attained. However, an accuracy of 1 per cent is desirable in the thickness measurements when the precision of the abrasion measurement is considered.

Effect of Film Thickness on Abrasion Value—Since varnishes were expected to show a non-linear relationship between film thickness and abrasion value, the three different varnishes were each spun to three different thicknesses and their abrasion value measured. The sample panels were allowed to age 18 days after preparation. The results are shown in Table VI.

Table VI—Effect of Film Thickness on Abrasion Value of Varnishes

Material	V-15			V-16			V-17		
Thickness:									
Mil	0.37	0.62	1.03	0.44	0.53	1.13	0.49	0.78	0.96
Cm. × 10^{-3}	0.94	1.58	2.62	1.12	1.35	2.87	1.25	1.98	2.44
Abrasion value, grams	45.2	90.0	151.1	67.0	82.7	192.6	86.9	164.9	255.0

Table IV, which contains the varnish formulas, and Table VI show that as the oil length of the varnish increases the deviation from a linear relation becomes more pronounced. This indicates that such films at this age had not dried through uniformly. However, the short length varnish V-15 showed practically a linear relation. In general, then, varnishes ought to be compared for abrasion value at comparable levels of thickness.

Effect of Age—In order to enhance the effect of aging, panels coated with all the materials under test were maintained at 60° C. (140° F.) in an air oven for a period of 5 weeks and then compared for abrasion value with freshly prepared films. All the coatings were approximately 0.0127 mm. (0.5 mil) in thickness. Table VII shows the results of the aging test.

Table VII—Effect of Aging on Abrasion Value

Material	Abrasion Value, Grams/0.0127 mm. Unaged film[a]	Aged film
L-20	54.8	45.5
L-21	38.9	33.6
L-22	41.3	35.8
V-15	79.2	67.0
V-16	93.0	87.6
V-17	118.8	101.0

[a] The lacquer films were 2 days old and the varnish 6 days; both were maintained at 70° F. (21.1° C.) and 65 per cent relative humidity prior to test.

Just how much the normal aging of these films was accelerated as the result of maintenance at the elevated temperature is conjectural. For either type of material, it will be observed that the change in abrasion value was not large. It is apparent, however, that the abrasion test reveals the effect of aging.

Effect of Temperature and Humidity of Air on Abrasion Value—The various films employed in the present investigation were allowed in different experiments to come to equilibrium with the air and were maintained at four different conditions of temperature and humidity. The values obtained for abrasion resistance are given in Table VIII.

Table VIII—Effect of Temperature and Moisture on Abrasion Value

Material	70° F. (21.1° C.) 41% R. H. *G./0.0127 mm.*	70° F. (21.1° C.) 65% R. H. *G./0.0127 mm.*	90° F. (32.2° C.) 41% R. H. *G./0.0127 mm.*	90° F. (32.2° C.) 90% R. H. *G./0.0127 mm.*
L-17	53.5	44.3	49.0	49.7
L-18	45.3	37.8	36.6	40.0
L-19	30.0	24.8	25.6	30.1
L-20	54.3	55.8	44.6	48.3
L-21	38.7	38.9	33.1	35.5
L-22	41.7	41.3	34.7	36.7
V-15	61.0	79.2	76.9	98.2
V-16	69.0	93.0	88.1	118.8
V-17	106.0	118.8	119.0	172.2
Baked varnish	88.0	78.6	82.5	95.6
Varnish enamel	61.4	58.2	62.5	81.6
Baked japan	77.4	66.4	66.4	68.8

It has been shown by Lowry and Kohman (*2*) that the quantity of water absorbed by rubber and paper from the atmosphere is approximately constant at various temperatures provided the relative humidity is held constant. It was assumed that the same relationship held true for paint films and a means was thereby afforded of separating the effect due to temperature changes from those due to changes in moisture of the film.

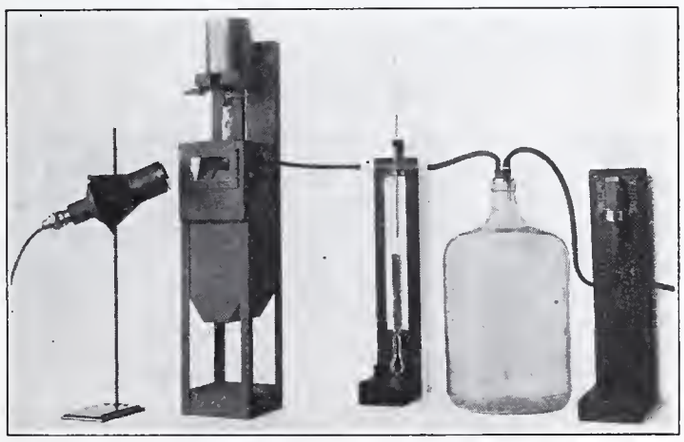


Figure 4—Apparatus for Measuring Abrasion Resistance

It was thought that it would be of interest to correlate the values for abrasion with those for hardness of the films under the above conditions of humidity and temperature. The Pfund hardness tester (*3*) was the instrument used for measuring hardness and, as is customary, the load required to give a diameter of impression of 3 units (in this case 0.3 mm.) on the vernier scale of the eyepiece was arbitrarily defined as hardness. The results are summarized in Table IX.

Table IX—Effect of Moisture and Temperature on Pfund Hardness

Material	70° F. (21.1° C.) 41% R. H. *G./0.3 mm.*	70° F. (21.1° C.) 65% R. H. *G./0.3 mm.*	90° F. (32.2° C.) 41% R. H. *G./0.3 mm.*	90° F. (32.2° C.) 90% R. H. *G./0.3 mm.*
L-17	1050	825	940	500
L-18	1185	850	1200	500
L-19	1000	900	900	500
V-15	500	380	200	2
V-16	285	235	80	10
V-17	150	40	20	4
Baked varnish	1500	1370	1360	900
Varnish enamel	425	265	235	12

The amberol lacquer series (L-20–L-22) showed cracking of the film when tested at the 70° F. and 41 per cent humidity condition and was therefore omitted.

Inspection of Tables VIII and IX leads to some interesting observations on the behavior of the materials with change in temperature and moisture content of the films.

Effect of Temperature—(*a*) The temperature coefficient of abrasion is greater for the varnishes than for the lacquers. At 41 per cent relative humidity, a change from 70° F. to 90° F. causes the varnishes to increase in abrasion resistance, while the lacquers, the japan, and the baked varnish decrease over the same range of temperature. The varnish enamel shows no temperature coefficient.

(*b*) All of the materials soften with increase in temperature, the change being greatest in the case of the varnishes.

Effect of Moisture—(*a*) The abrasion values for the varnishes increase markedly with increase in moisture content of the films, the change becoming more pronounced with increasing oil lengths. For example, the longest oil varnish tested, V-17, displays an increase in abrasion value of 45 per cent at 32.2° C. (90° F.) over the range of humidities investigated.

(*b*) The amberol lacquers show only a slight increase in abrasion resistance with increase in humidity, while the ester gum lacquers, the japan, and the baked varnish appear to pass through a minimum abrasion value in the neighborhood of 65 per cent relative humidity.

(*c*) The hardness for all the materials decreases definitely as the films take up moisture.

(*d*) The spread of hardness values for the varnishes is greater at the lower humidities, the values tending to converge as the films absorb moisture.

Precision of the Method

In general, the precision of the present test is governed by the uniformity of the film and the accuracy with which its thickness can be measured. A series of 116 different abrasion determinations on various films of fairly good thickness uniformity gave, on omitting the thickness factor, the following distribution of per cent deviations from the mean value:

No. of Detns.	Deviation Limits %
46	0.0 to 0.5
24	0.5 to 1.0
28	1.0 to 2.0
16	2.0 to 3.0
2	3.0 to 4.0

The average per cent deviation of these determinations was 0.99.

To illustrate how the precision of the abrasion determinations depends on the smoothness of the film surface, a series of lacquers that exhibited an orange peel surface, when re-spun with a slow evaporating solvent to eliminate orange peel effect, gave the reduction of the average per cent deviation from the mean value from 6.2 to 0.6 per cent.

Investigation showed that the method of illumination—i.e., whether from the rear or from the front—has very little effect upon the attainable precision. The choice of a relatively large bare area, 2 mm. in diameter, for the end point, rather than the first appearance of tiny pinholes was influenced by the fact that the larger area is more representative of the film as a whole. The high order of precision which was obtained in the application of the test justifies this choice of end point. It was found that the time difference between the first pinhole and the end point selected, increased as the total time required for the test increased.

Discussion

The method of measuring abrasion resistance described in the present paper should provide a useful tool of high precision in research on the formulation of paint materials. Since this method concerns itself primarily with cohesional characteristics of materials it may be used to study the influence of composition on those qualities related to cohesion. A more definite interpretation of the fundamental significance of this test should be obtained in the study now under way in which it is sought to correlate abrasion and hardness with tensile strength and elongation.

The direct application of the test to paint films with a view to correlating the abrasion values as measured with service performance still requires considerable study, since abrading forces in service produce wear degradations in a variety of ways. A direct application of the test in the form described may be in the evaluation of the relative abrasion resistance of paint, lacquer, and varnish films when used in the airplane industry. No question of significance need arise in this application, since the air speeds in service and in the test are comparable and it has been shown that relative concentration of abrading particles is negligible when distributed randomly. Quite likely, by a suitable choice of air pressures, particle sizes, and particle concentrations, other typical forms of wear action by forces of abrasion can be made to simulate service conditions, in that manner simplifying the problem of interpretation of the test for practical purposes.

As mentioned previously in this paper, the test is not restricted to the evaluation of abrasion resistance of paint materials. For instance, it has been found that various electroplated metals, chromium, zinc, and cadmium, gave a wide range of values for abrasion resistance with a high degree of duplicability. It seems likely that this method may serve as an effective means of investigation of the wearing quality of electrodeposits.

Literature Cited

(1) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours," 4th ed., Institute of Paint and Varnish Research, 1927.
(2) Lowry, H. H., and Kohman, G. T., *J. Phys. Chem.*, **31**, 23–57 (1927).
(3) Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **25**, 393 (1925).

Alcohol Replacing Gasoline in Brazil—Among the methods used in Brazil to encourage the use of alcohol motor fuel instead of gasoline is a 50 per cent reduction in tariff fines in the City of Maceio to motorists using the fuel, according to a statement by the Department of Commerce.

The alcohol fuel is a domestic Brazilian product made from sugar waste and is being marketed in competition with imported gasoline, a considerable part of which comes from the United States. The retail price of gasoline during the third quarter of the year in Rio de Janeiro ranged from 40 to 45 cents, according to the department.

In the Pernambuco area of Brazil gasoline sales have been greatly reduced in recent months and importations have correspondingly decreased. United States exports of gasoline to Brazil during the first nine months of 1930 exceeded 1,000,000 barrels, which was nearly equal the amount of the corresponding period of 1929. Exports during the month of October, however, were slightly more than 14,000 barrels as compared with more than 120,000 barrels in the same month of a year ago.

Whether alcohol motor fuel will be able to maintain itself as a satisfactory substitute for gasoline cannot be settled until the public has learned its effect on motors and carburetors; whether it is more economical and whether it develops satisfactory power.

The Iodide Method for Copper[1]

Bartholow Park

Michigan College of Mining and Technology, Houghton, Mich.

In the presence of much arsenic the usual iodide method for copper gives high results. By increasing the pH of the solution during the titration the action of arsenic acid on potassium iodide is retarded, but so is the action of copper. Maximum pH values at which cupric ion is completely reduced by iodide ion have been determined. These pH values vary with different acids because of the formation of insoluble or slightly ionized compounds of copper. The maximum pH value at which arsenic acid liberates iodine from potassium iodide solutions has been determined.

General equations for the calculation of the electrode potentials of solutions of arsenic and arsenious acids and of solutions of iodine and iodide have been developed. The theoretical maximum pH value at which arsenic acid liberates iodine from potassium iodide solution has been calculated and shown to agree substantially with the value obtained by experiment.

A solution containing copper, arsenic acid, and potassium biphthalate may be adjusted to a pH value at which all of the copper but none of the arsenic will react with iodide.

The action of ferric iron on potassium iodide may be completely suppressed, in the absence of manganese, by the addition of ammonium bifluoride.

A very short and accurate method for determining copper in ores, slags, mattes, etc., has been developed from the above considerations.

A COMPREHENSIVE survey of the literature pertaining to the iodide method for copper disclosed the following facts:

When a solution of cupric ion is treated with an excess of potassium iodide, the following reaction takes place:

$$2Cu^{++} + 4I^{-} = 2CuI + I_2$$

The liberated iodine may be reduced to iodide ion by the action of standard sodium thiosulfate solution and the quantity of copper calculated, providing that the reaction proceeds quantitatively to the right, no other substance which oxidizes iodide ion to iodine is present, and no substance which reduces free iodine to iodide ion is present.

Ferric iron will liberate iodine, and, as it is almost always present in copper ores, provision must be made for removing it or rendering it inactive. In Low's iodide method (*14*) iron is separated from copper by means of aluminum. In Mott's short iodide method (*15*) it is changed to ferric fluoride, which has no effect on potassium iodide on account of the very slight dissociation of this substance.

Arsenic in its trivalent form reduces free iodine, and in strongly acid solutions pentavalent arsenic liberates iodine from potassium iodide. No provision for removing arsenic is made in either of the above methods. Low in his method states that arsenic is without effect.

The following questions were selected for more detailed study:

(1) Under what conditions do arsenic and antimony liberate iodine from iodides?

(2) What hydrogen-ion concentration is best for the reaction between cupric ion and iodide ion, and how may this optimum concentration be obtained?

(3) Is it necessary to remove iron, and if not what is the best method for preventing its action on iodides?

Effect of Arsenic on Iodide Method for Copper

Experiments were made to find out whether or not arsenic affects either Low's or Mott's method. The results are given in Table I. In each case 50 cc. of copper sulfate solution containing 0.2 gram of copper were carefully measured with a pipet, and acetic acid and ammonium bifluoride were added in the proportions noted. To some of the samples arsenic acid solution was added. Then 3 grams of potassium iodide were put into each, and the liberated iodine titrated with standard thiosulfate solution. Each result is the mean of two or more titrations. Evidently pentavalent arsenic does have an effect upon either the long or the short iodide method. In the last two experiments the blue color returned within 2 or 3 minutes after the end point had been reached.

Table I—Effect of Arsenic on Low's and Mott's Method

Copper Taken	16 *N* Acetic Acid	Ammonium Bi-fluoride	Potassium Iodide	Arsenic	Copper Found
Gram	*Cc.*	*Grams*	*Grams*	*Gram*	*Gram*
0.2000	10	...	3	...	0.2000
0.2000	5	...	3	...	0.2000
0.2000	5	...	3	0.1	0.2010
0.2000	5	...	3	0.2	0.2015
0.2000	2	2	3	0.2	0.2015

More detailed information than could be found in the literature (*1*, *3*, *6–8*, *11*, *12*, *16–22*) was desired on the reaction between arsenic acid and iodide ion and a series of experiments to determine the extent of this reaction at various hydrogen-ion concentrations was undertaken.

Solutions containing a constant amount of arsenic acid at different hydrogen-ion concentrations were prepared. A measured quantity of potassium iodide solution was added to each, and at the end of 5 minutes the liberated iodine was determined by titration with dilute thiosulfate. The results are given in Table II and Figure 1.

Table II—Reaction between Arsenic Acid and Iodide Ion at Various pH Concentrations

Arsenic Taken	pH of Solution	Thiosulfate	Arsenic Reduced
Gram		*Cc.*	%
0.0230	2.51	1.55	0.219
0.0230	2.61	1.30	0.184
0.0230	2.85	1.14	0.161
0.0230	2.93	1.01	0.143
0.0230	3.12	0.90	0.127
0.0230	3.33	0.70	0.099
0.0230	3.64	0.50	0.072
0.0230	4.77	None	None

In all of the titrations 10 cc. of arsenic acid in potassium biphthalate buffer solution were treated with 3 cc. of potassium iodide solution containing 2 grams of potassium iodide. After 5 minutes 1 cc. of starch solution was added, and the liberated iodine titrated with dilute thiosulfate solution, 1 cc. of which was equivalent to 0.00003 gram of arsenic. The duration of the titration was 1 minute. By means of the quinhydrone electrode the hydrogen-ion concentration was determined on another portion of each arsenic-

[1] Received September 12, 1930. A thesis submitted for the degree of master of science in chemistry at the Michigan College of Mining and Technology.

phthalate solution before the addition of potassium iodide.

Another set of solutions was prepared in which phosphate buffers were substituted for phthalate solutions. These were titrated as before, and the curve obtained from plotting the results was practically the same as that given in Figure 1.

The reaction may be written

$$H_3AsO_4 + 2HI = H_3AsO_3 + I_2 + H_2O$$

or, assuming the existence of the triiodide ion

$$H_3AsO_4 + 3HI = H_3AsO_3 + HI_3 + H_2O$$

In addition to the hydrogen-ion concentration, the iodine and iodide concentrations, the temperature, and the time all affect the amount of iodine liberated by a given weight of arsenic. Table II and Figure 1 show only the trend. It should be noted that under the usual conditions of acidity prevailing in the final solution when copper is being determined by the iodide method, any arsenic present will not start to react until most of the iodine has been titrated.

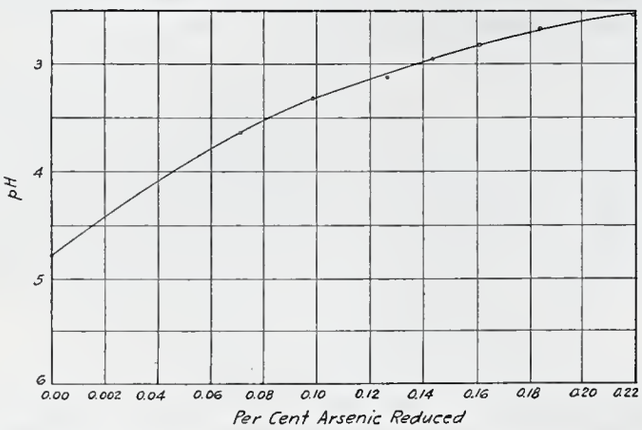


Figure 1—Liberation of Iodine at Various pH Concentrations

As the titration is usually performed rather rapidly, any arsenic present will not have a chance to react with iodide ion for a long enough time to reach equilibrium. A reaction period of 5 minutes was arbitrarily chosen for the experiments listed in Table II. This period was thought to represent the usual length of time during which arsenic would have a chance to react while a titration was being performed. The concentration of potassium iodide in all of these experiments with arsenic was greater than it would ordinarily be in a copper titration. Nevertheless, it appears that at the usual acidities and concentrations occurring in the iodide method, arsenic, if present, is a distinct menace to the accuracy of the copper determination.

Similar buffer solutions were prepared from antimony, and the results of titration were plotted as before. The curve obtained was practically the same as that given for arsenic in Figure 1.

Another series of experiments was carried out in the following manner: Ten cubic centimeters of arsenious acid solution containing sodium carbonate, potassium biphthalate, and a little starch were treated with a solution of iodine in potassium iodide until the blue starch-iodine color just appeared. One drop of arsenious acid solution was added, which discharged the color. Dilute sulfuric acid was added 1 cc. at a time to the colorless solutions and pH determined after each addition until the blue color reappeared. Duplicate determinations gave pH 3.65 and pH 3.50 as the points at which the blue first became apparent.

These experimental results are in substantial agreement with the results predicted theoretically by the oxidation-reduction potentials of the iodine-iodide and the arsenic-arsenious couples, as is shown below.

Oxidation-Reduction Potentials of Arsenic-Arsenious Solutions

The reaction of arsenic acid acting as an oxidizing agent or of arsenious acid acting as a reducing agent may be formulated thus:

$$HAsO_4^{--} + 2e + 4H^+ \rightleftharpoons H_3AsO_3 + H_2O$$

The ionization constants for the third step in the ionization of arsenic acid and for the first step in the ionization of arsenious acid are practically the same (*2, 5, 9, 24, 25*) and therefore they need not be considered in the treatment which follows.

The equilibrium state may be formulated thus:

$$\frac{(HAsO_4^{--})\,(e)^2\,(H^+)^4}{(H_3AsO_3)} = K \qquad (1)$$

from which

$$e = \sqrt{\frac{K(H_3AsO_3)}{(H^+)^4\,(HAsO_4^{--})}}$$

substitution of this value of (e) in the general electrode equation (*4*)

$$E = \frac{RT}{F}\ln(e_m) - \frac{RT}{F}\ln(e_s) \qquad (2)$$

in which (e_m) and (e_s) represent the electron concentrations in the metallic electrode and the solution gives:

$$E = \frac{RT}{F}\ln(e_m) - \frac{RT}{F}\ln\sqrt{\frac{K(H_3AsO_3)}{(H^+)^4\,(HAsO^{4--})}} \qquad (3)$$

Rearrangement and combination of constants gives

$$E = C + \frac{2RT}{F}\ln(H^+) - \frac{RT}{2F}\ln\frac{(H_3AsO_3)}{(HAsO_4^{--})} \qquad (4)$$

It is convenient to have the expression in terms of the total concentrations of arsenic and arsenious acid present instead of in terms of the ion concentrations. In solution the total reductant, *Sr*, may be assumed to equal the concentration of arsenious acid, and the total oxidant, *So*, may be assumed to be given by the sum of the concentrations of the various ions and unionized substances containing pentavalent arsenic.

$$So = (HAsO_4^{--}) + (H_2AsO_4^-) + (H_3AsO_4) \qquad (5)$$

The equilibrium equations for the first and second steps in the ionization of arsenic acid are

$$\frac{(H_2AsO_4^-)\,(H^+)}{(H_3AsO_4)} = Ko_1 \qquad \frac{(HAsO_4^{--})\,(H^+)}{(H_2AsO_4^-)} = Ko_2 \qquad (6)$$

Substitution of values obtained from these equations in Equation 5 gives

$$So = (HAsO_4^{--}) + \frac{(HAsO_4^{--})\,(H^+)}{Ko_2} + \frac{(HAsO_4^{--})\,(H^+)^2}{Ko_1\,Ko_2} \qquad (7)$$

from which

$$(HAsO_4^{--}) = So\,\frac{Ko_1\,Ko_2}{Ko_1\,Ko_2 + Ko_1\,(H^+) + (H^+)^2}$$

Substitution of this value of ($HAsO_4^{--}$) and of *Sr* for (H_3AsO_3) in Equation 4 gives

$$E = C + \frac{2RT}{F}\ln(H^+) - \frac{RT}{F}\ln\frac{Sr}{So} - \frac{RT}{F}\ln\frac{Ko_1\,Ko_2 + Ko_1\,(H^+) + (H^+)^2}{Ko_1\,Ko_2} \qquad (8)$$

At 25° C. $\frac{RT}{F}$ ln is equal to

$$\frac{1.9885 \times 298 \times 2.3026}{23074} \log = 0.059 \log$$

Ko_1 is about 5×10^{-3} (*23*) and Ko_2 is about 4×10^{-5} (*2*) depending upon the concentration of the arsenic acid.

Substituting these values in Equation 8 and remembering that $-\log (H^+) = pH$ we get

$$E = C - 0.118\ pH - 0.0295 \log \frac{Sr}{So} - 0.0295 \log \frac{2 \times 10^{-7} + 4 \times 10^{-5} (H^+) + (H^+)^2}{2 \times 10^{-7}} \quad (9)$$

Equation 9 is the general equation for the electrode potential, E, of any solution containing arsenic and arsenious acids.

Washburn and Strachan (*23*) found that, when the activities of arsenic acid, arsenious acid, and hydrogen ion are all equal to unity, E equals 0.574 volt. Substitution of these values in Equation 9 gives

$$0.574 = C - 0.197 \text{ or } C = 0.771 \quad (10)$$

The complete general equation is therefore

$$E = 0.771 - 0.118\ pH - 0.0295 \log \frac{Sr}{So} - 0.0295 \log \frac{2 \times 10^{-7} + 4 \times 10^{-5} (H^+) + (H^+)^2}{2 \times 10^{-7}} \quad (11)$$

which may be used to calculate the potential of any mixture of arsenic and arsenious acids at any hydrogen-ion concentration. An alternate method of calculating the value of C follows.

When equilibrium is reached in the reaction between arsenic acid and iodide, the equation may be written

$$HAsO_4^{--} + 3I^- + 4H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$$

and the following relationship holds

$$\frac{(HAsO_4^{--})\ (I^-)^3\ (H^+)^4}{(H_3AsO_3)\ (I_3^-)} = K \quad (12)$$

This may be combined with Equation 6 to give

$$\frac{(H_3AsO_4)\ (I^-)^3\ (H^+)^2}{(H_3AsO_3)\ (I_3^-)} = K^1 \quad (13)$$

Washburn and Strachan calculated the value of K^1 from seven equilibrium experiments and found an average at 25° C. of 5.54×10^{-2}. They also found that in the following equilibrium K has a value of 1.3×10^{-3} at 25° C.

$$\frac{(I^-)\ (I_2)}{(I_3^-)} = K = 1.3 \times 10^{-3}$$

or

$$(I_3^-) = \frac{(I^-)\ (I_2)}{1.3 \times 10^{-3}} \quad (14)$$

Substitution of these values in Equation 13 gives

$$\frac{(H_3AsO_4)\ (I^-)^2\ (H^+)^2}{(H_3AsO_3)\ (I_2)} = 42.6 \quad (15)$$

The average value of Ko_1 in Washburn and Strachan's experiments was 5.6×10^{-3}. When this value and that of Ko_2 given previously are substituted in Equation 6,

$$(H_3AsO_4) = \frac{(HAsO_4^{--})\ (H^+)^2}{2.25 \times 10^{-7}}$$

Substitution of this value in Equation 15 gives

$$\frac{(HAsO_4^{--})\ (I^-)^2\ (H^+)^4}{(H_3AsO_3)\ (I_2)} = 9.6 \times 10^{-6} \quad (16)$$

The general electrode equation for the arsenic-arsenious couple, Equation 3, may be put in the following form:

$$E_{As} = C + 0.0295 \log \frac{(HAsO_4^{--})\ (H^+)^4}{(H_2AsO_3)}$$

The equation for the iodine-iodide couple, as will be shown later, is

$$E_I = 0.6211 - 0.0295 \log \frac{(I^-)^2}{(I_2)}$$

At equilibrium $E_{As} = E_I$ and

$$C + 0.0295 \log \frac{(HAsO_4^{--})\ (H^+)^4}{(H_3AsO_3)} = 0.6211 - 0.0295 \log \frac{(I^-)^2}{}$$

$$0.6211 - C = 0.0295 \log \frac{(HAsO_4^{--})\ (I^-)^2\ (H^+)^4}{(H_3AsO_3)\ (I_2)}$$

$$= 0.0295 \log 9.6 \times 10^{-6}$$

from which $C = 0.769$

Table III contains values of E calculated from Equation 11 at different hydrogen-ion concentrations when $\frac{Sr}{So}$ has the values given in columns 2, 3, and 4, respectively.

Table III—Calculated Values of E under Different Conditions

pH	$E\ \frac{Sr}{So} = 1$	$E\ \frac{Sr}{So} = \frac{1}{1000}$	$E\ \frac{Sr}{So} = \frac{1}{10,000}$
0	0.574	0.663	0.692
0.5	0.544	0.633	0.662
1.0	0.515	0.603	0.633
1.5	0.485	0.573	0.603
2.0	0.456	0.544	0.574
2.5	0.425	0.514	0.543
3.0	0.394	0.482	0.512
3.5	0.353	0.441	0.471
4.0	0.298	0.387	0.416
4.5	0.241	0.330	0.359
5.0	0.181	0.270	0.299
6.0	0.062	0.151	0.180

Oxidation-Reduction Potentials of Iodine-Iodide Solutions

The reduction of triiodide ion to iodide ion may be formulated

$$I_3^- + 2e \rightleftharpoons 3I^-$$

The equilibrium state may be formulated thus

$$\frac{(I_3^-)\ (e)^2}{(I^-)^3} = K$$

or

$$(e) = \sqrt{\frac{(I^-)^3\ K}{(I_3^-)}} \quad (17)$$

Substitution of this value of (e) in the general electrode equation (2) gives

$$E = C - 0.059 \log \sqrt{\frac{(I^-)^3\ K}{(I_3^-)}} \quad (18)$$

from which, by rearranging and combining constants,

$$E = C' - 0.0885 \log (I^-) + 0.0295 \log (I_3^-) \quad (19)$$

The equilibrium between free iodine, iodide ion, and triiodide ion may be formulated thus

$$\frac{(I_2)\ (I^-)}{(I_3^-)} = K \quad (20)$$

Substituting the value of (I_3^-) obtained from this equation in the electrode equation (19) and combining terms,

$$E = C'' - 0.059 \log (I^-) + 0.0295 \log (I_2) \quad (21)$$

This is the equation relating E with the activities of iodide ion and iodine in any solution. Jones and Kaplan (*10*) have found that, when the iodide ion has unit activity and the iodine concentration (I_2) is a constant and equal to the solubility (0.00132 molar at 25° C.), the normal potential e_o is 0.5362 against the hydrogen electrode. The following equation represents their findings for the saturated I_2 electrode:

$$E = 0.5362 - 0.059 \log (I^-) \qquad (22)$$

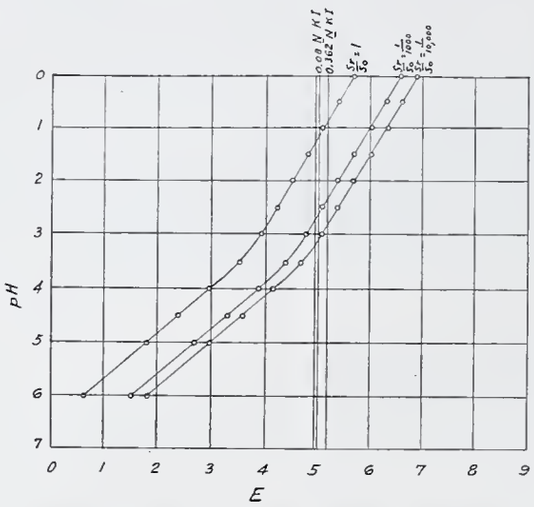


Figure 2—Values of *E* under Various Conditions

When the activity of the iodide ion is unity and the solution has an iodine concentration of 1.32×10^{-3} gram-mols per liter, the general equation (21), derived above, takes the following form, assuming that the activity coefficient of the free iodine is one:

$$E = C'' + 0.0295 \log 1.32 \times 10^{-3} = 0.5362 \qquad (23)$$

from which $C'' = 0.6211$. The following equation represents the relationship between E and the activities of both iodide ion and iodine:

$$E = 0.6211 - 0.059 \log (I^-) + 0.0295 \log (I_2) \qquad (24)$$

Values of E for several concentrations of iodide and iodine have been calculated in the following manner: Taking for the concentration of free iodine the smallest amount detectable with starch—i. e., 2.5×10^{-5} gram-mols per liter (*13*)—and again assuming that its activity coefficient is one, the equation becomes

$$E = 0.6211 - 0.059 \log (I^-) + 0.0295 \log 2.5 \times 10^{-5}$$

or

$$E = 0.4851 - 0.059 \log (I^-) \qquad (25)$$

When a solution contains 3 grams of potassium iodide in 50 cc., it is 0.362 normal. Using Jones and Kaplan's constants and Bronsted's equation to solve for the activity coefficient, f, gives

$$\log f = -0.373 \sqrt{0.362} + 0.125 \times 0.362 = -0.1789 \qquad (26)$$

from which $f = 0.66$.

The E value of a solution 0.362 normal with respect to potassium iodide and containing just enough free iodine to give a visible color with starch is given by the following equation:

$$E = 0.4851 - 0.059 \log 0.362 - 0.059 \log 0.66 \qquad (27)$$

from which $E = 0.522$ volts. Similarly the E value of a solution containing 2 grams of potassium iodide in 15 cc. is $E = 0.5045$.

These values do not change with changes in the hydrogen-ion concentration. In Figure 2 are plotted the results tabulated in Table III, together with the oxidation-reduction curves, in this case straight lines, for the iodine-iodide solutions mentioned above.

When conditions are such that a point on the curve for arsenic lies to the right of the curve for iodine, there is a tendency for free iodine to be liberated. At pH 2.85 a solution which is 0.36 normal with respect to potassium iodide is in equilibrium with a solution which contains practically all of its arsenic in the pentavalent state only when there is a detectable quantity of free iodine in the solution. When stronger solutions of potassium iodide are present, the pH at equilibrium must be correspondingly greater.

It seems advisable, therefore, from a theoretical standpoint to keep the pH of the solution at 3.5 or above during the titration of copper when arsenic is present in order to prevent the liberation of iodine by arsenic.

Effect of Hydrogen-Ion Concentration on Reaction between Cupric Ion and Iodide Ion

A series of titrations was carried out to determine the effect of ammonium acetate on the reaction between cupric ion and iodide ion. The results are given in Table IV.

Table IV—Effect of Ammonium Acetate on Reaction

Copper Taken	16 *N* Acetic Acid	15 *N* Ammonium Hydroxide	Potassium Iodide	Copper Found
Gram	*Cc.*	*Cc.*	*Grams*	*Gram*
0.2000	..	...	3	0.2000
0.2000	5	1	3	0.2003
0.2000	5	2	3	0.2003
0.2000	5	3	3	0.2000 slow
0.2000	10	5	3	0.1995 very slow

In the fourth titration the end point was slow in appearing. The blue color would reappear after having been discharged. The same difficulty was experienced to a much greater extent in the fifth titration, the time required for this titration being about 20 minutes. This behavior was due to the decreased speed of reaction between cupric ion and iodide ion which in turn was probably caused by the lower hydrogen-ion concentration and the decrease in activity of the cupric ion, both of which were brought about by the large amount of acetate ion present. The results show that although a small amount of ammonium acetate does no harm, large amounts should be avoided.

It was next decided to determine whether or not copper could be titrated at a low enough hydrogen-ion concentration to preclude the effects due to arsenic. Buffer solutions containing copper at constant concentration, salts at constant concentration, and varying hydrogen-ion concentration, were prepared and after addition of potassium iodide, were titrated. The results are given in Table V and Figure 3.

Table V—Titration of Copper in Various Buffer Solutions

Tartrate		Citrate		Phosphate		Acetate		Phthalate	
pH	% Cu	pH	% Cu	pH	% Cu	pH	% Cu	pH	% Cu
2.08	100	2.14	100	3.21	100	4.27	100	5.50	100
2.36	100	2.44	100	3.64	100	4.45	100	5.70	100
2.51	79[a]	2.81	98.3[a]	3.80	90[a]	4.63	99.4	5.83	98.0
2.64	71[a]	2.96	96.5[a]	3.84	89[a]	4.71	94.8	5.96	96.0
2.86	60[a]	3.15	93.4[a]	3.74	79[a]	4.78	92.1	6.24	91.5
3.16	50[a]	3.33	85.6[a]			4.95	85.1	6.23	87.0[a]
3.47	34[a]	3.52	70.8[a]			5.15	79.0[a]	6.28	83.0[a]
		3.73	57.8[a]			5.15	66.0[a]	6.32	77.5[a]
		3.96	45.6[a]			5.15	63.0[a]	6.34	73.1[a]
		4.48	20.5[a]					6.45	65.9[a]
								6.76	39.0[a]

[a] Precipitates.

Each of the solutions listed in Table V was 0.0375 molar in acid concentration and 0.015733 molar in copper sulfate. The same technic was employed in mixing the various solutions. After mixing, the pH was determined on a portion of the solution by means of the quinhydrone electrode. In

a large number of the solutions, precipitates formed and the low percentage of copper found by titration was due at least partially to them. At first attempts were made to titrate the copper in the precipitates by allowing them plenty of time to dissolve after the titration had been started. This plan was changed later to the less representative but more practical plan of allowing the precipitates to settle and pipetting off the clear liquid for titration. The latter method gives practically the same results on account of the very slow solubility of the precipitates. Five cubic centimeters of the clear solution were pipetted off into a small beaker. Two cubic centimeters of potassium iodide solution, containing 1 gram of potassium iodide, were added and the solution was titrated with dilute thiosulfate solution in the usual manner. The per cent of copper titrated under these conditions was calculated and plotted against the pH of the solution.

From an inspection of Figure 3 it appears that the amount of copper which enters into reaction with potassium iodide depends upon the nature of the acid present as well as upon the hydrogen-ion concentration. This is due in some cases, noted above, to the formation of insoluble copper salts, but in those cases where no precipitates appeared the explanation is not so apparent. The assumption of the formation of unionized or slightly ionized copper compounds is one way out of the difficulty. This also accounts for the effect of ammonium acetate in the usual method. (As the amount of acetate ion increases, the amount of undissociated cupric acetate increases and the amount of cupric ion decreases, thereby slowing up the reaction between cupric ion and potassium iodide.)

From an inspection of Table V and Figure 3 it is apparent that phthalic acid is better than acetic for the iodide determination when arsenic is present.

Fluoride-Phthalate-Iodide Method for Copper

A method for the determination of copper in ores, mattes, slags, etc., containing arsenic or antimony, has been developed in which potassium biphthalate is used to buffer the solution. Ammonium bifluoride is added to inhibit the reaction between ferric iron and iodide. That it really has such an effect is shown by the results of several titrations given in Table VI.

Table VI—Effect of Iron in Presence of Fluoride

Copper Taken	Iron	Ammonium Bifluoride	16 N Acetic Acid	Copper Found
Gram	*Gram*	*Grams*	*Cc.*	*Gram*
0.2000	0.02	1	5	0.2000
0.2000	0.10	1	5	0.2000
0.2000	0.20	2	5	0.1999
0.2000	0.30	2	5	0.2002

Treat a suitable sample of ore, slag, etc., with nitric acid until all copper is in solution. Boil down to about 5 cc., add 30 cc. of water, and boil to assure complete solution of soluble matter and also to expel oxides of nitrogen. Filter and wash the residue well with hot dilute nitric acid. If the residue is small in amount or light-colored, filtration may be omitted. Concentrate the solution by boiling to about 30 cc., cool, add ammonium hydroxide until the iron is all precipitated and the solution smells faintly of ammonia. Avoid adding an excess. Add 2 grams, weighed, of ammonium bifluoride, shake, add 1 gram, weighed, of potassium biphthalate, shake, add 3 grams, weighed, of potassium iodide, shake. Titrate at once with thiosulfate, approaching the end point slowly. When near the end point, add sufficient starch solution. After the blue color has been completely discharged, it should not return within 30 minutes at least.

If the copper is not all taken into solution by nitric acid, some other method must be employed, in which case 10 cc. of bromine water should be added with the 30 cc. of water above to assure complete oxidation of arsenic and antimony, and the boiling continued until all of the free bromine has been expelled. When a mixture containing pentavalent arsenic or antimony and free sulfur is taken to fumes of sulfuric acid, the sulfur acts in much the same manner as organic matter would and reduces the arsenic and antimony to the trivalent state.

Addition of potassium biphthalate to the approximately neutral solution fixes the pH at about 4. Here copper will react with potassium iodide but pentavalent arsenic and antimony will not.

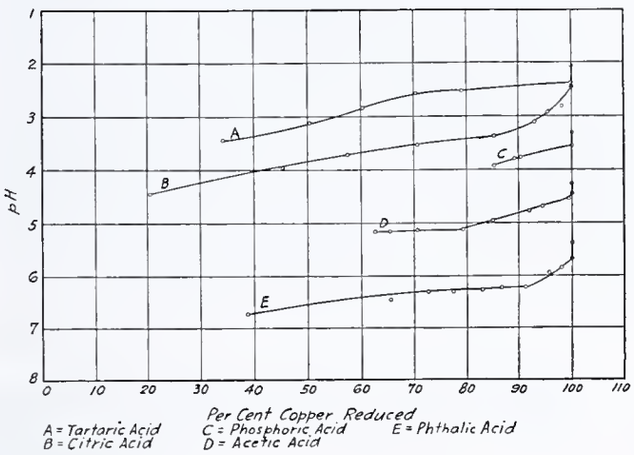


Figure 3—Titration of Copper in Various Buffer Solutions

In the presence of large amounts of iron or aluminum more ammonium bifluoride must be added. Aluminum forms an insoluble fluoride which, when present in large amounts, occludes some copper and slows up the titration. Approximately 1 gram of ammonium bifluoride should be added for each 0.1 gram of iron or aluminum, but the accuracy of the method decreases as the amount of iron increases. A quick return of the blue color may be due to insufficient ammonium bifluoride.

Table VII—Effect of Impurities on Method

Impurity		pH at E. P.	Copper Found
		Iron	
Gram			*Gram*
Fe			
0.1		4.3	0.1998
0.1		4.0	0.2001
0.1		4.1	0.2001
		Arsenic	
As			
0.1		4.3	0.1997
0.1		3.9	0.2002
		Iron and arsenic together	
Fe	As		
0.1	0.1	4.10	0.2002
0.2	0.2	3.82	0.2000
0.2	0.4	3.95	0.2002
0.1	0.1	3.90	0.2000
		Manganese alone and with iron	
Fe	Mn		
...	0.1	4.16	0.2007
...	0.1	4.10	0.2000
...	0.1	4.51	0.1993
...	0.1	4.10	0.2000
0.1	0.1	4.10	0.2020
0.1	0.1	4.13	0.2020
0.1	0.1	4.06	0.2021
0.1	0.01	4.10	0.2007
0.2	0.1	4.50	0.2060

An excess of ammonium hydroxide should be avoided, as it lowers the hydrogen-ion concentration and decreases the rate of reaction between copper and potassium iodide. A quick return of the blue color after it has been completely discharged may be due to insufficient acidity.

Oxides of nitrogen and free bromine, if present in the solution when potassium iodide is added, will cause results to run high and may cause a return of the blue after the end point has been reached.

The precipitate of ferric hydroxide should dissolve completely when shaken with ammonium bifluoride. If it does not, either too much ammonium hydroxide or too little ammonium bifluoride was added.

The results given in Table VII were obtained by treating a copper sulfate solution of 0.2 gram of copper containing the indicated impurities by the above method. The pH values of the solutions at the end point were determined by means of the quinhydrone electrode.

From an inspection of the results given in Table VII it is apparent that neither iron nor arsenic affect the copper value, as determined by this method, except in the presence of manganese. Manganese probably acts as catalyst for the reaction between ferric iron and iodide and speeds it up to such an extent that the fluoride present is not capable of completely preventing it. Fortunately manganese is not a common impurity in copper ores. When it is present, iron must be removed before the addition of ammonium hydroxide by one of the well-known methods.

Literature Cited

(1) Bassett, "Theory of Quantitative Analysis," p. 265, Rutledge, 1925.
(2) Blanc, *J. chim. phys.*, **18**, 28 (1920).
(3) Bray, *J. Phys. Chem.*, **6**, 365 (1902).
(4) Clark, U. S. Pub. Health Service, *Pub. Health Repts.* **38**, 443–55 (1923).
(5) Dhar, *Z. anorg. allgem. Chem.*, **153**, 330 (1926).
(6) Fleury, *Bull. soc. chim.*, **27**, 490 (1920).
(7) Foerster and Pressprich, *Z. Elektrochem.*, **33**, 176 (1927).
(8) Goard and Rideal, *Proc. Roy. Soc. (London)*, **105A**, 135 (1924).
(9) Hughes, *J. Chem. Soc.*, **491** (1928).
(10) Jones and Kaplan, *J. Am. Chem. Soc.*, **50**, 2066 (1928).
(11) Kolthoff, *Pharm. Weekblad*, **56**, 621 (1919).
(12) Kolthoff, *Z. anal. Chem.*, **60**, 393 (1921).
(13) Kolthoff and Furman, "Volumetric Analysis," Vol. II, p. 350, Wiley, 1929.
(14) Low, "Technical Methods of Ore Analysis for Chemists and Colleges," Wiley, 1927.
(15) Mott, *Chemist-Analyst*, **1912**, 5–7.
(16) Pedersen and Bjergaard, *Dansk Tids. Farm.*, **2**, 1–7 (1928); *C. A.*, **22**, 1116 (1928).
(17) Roebuck, *J. Phys. Chem.*, **6**, 365 (1902).
(18) Roebuck, *Ibid.*, **9**, 727 (1905).
(19) Rosenthaler, *Z. anal. Chem.*, **45**, 596 (1906).
(20) Thiel and Meyer, *Ibid.*, **55**, 177 (1916).
(21) Washburn, *J. Am. Chem. Soc.*, **30**, 31 (1908).
(22) Washburn and Strachan, *Ibid.*, **35**, 681 (1913).
(23) Washburn and Strachan, *Ibid.*, **35**, 694 (1913).
(24) Wood, *J. Chem. Soc.*, **93**, 411 (1908).
(25) Zawidzky, *Ber.*, **36**, 1427 (1903).

Potentiometric Determination of Acidity in Insulating Oils[1]

R. N. Evans and J. E. Davenport

Research Bureau, Brooklyn Edison Company, Inc., Brooklyn, N. Y.

The estimation of acidity in oils employing the alkali blue procedure has been found to give more satisfactory results than the A. S. T. M. procedure. In the latter method, methyl alcohol should not be substituted for ethyl alcohol.

Electrometric titrations have been carried out on type organic acids successfully.

The silver–silver chloride electrode can be used satisfactorily in routine determination of acidity. The most important disadvantage of the electrometric procedure is the time required. It is recommended that a preliminary approximate titration be carried out.

IN THE past the determination of acidity in oils has been accomplished generally by a procedure similar to that outlined in the A. S. T. M. Tentative Standards 1929, page 397. Recently Seltz and McKinney (*5*) described a quinhydrone-potentiometric method employing amyl alcohol as a solvent, lithium chloride as the conducting salt, and a boundary of agar-agar containing lithium chloride to separate the reference electrode from the solution under investigation. Later, Seltz and Silverman (*6*) eliminated the agar-agar boundary and substituted the silver–silver chloride electrode as the reference electrode. A comprehensive survey of the past work on potentiometric titration may be had by reference to a paper by Furman (*2*).

The following paper deals with the comparison of the electrometric method and several other procedures, employing indicators in which known acids were dissolved in a transformer oil. Many factors influencing the electrometric titration have also been experimentally studied.

Apparatus

The diagrammatic arrangement of the electrometric apparatus may be obtained by reference to the previously mentioned paper by Seltz and McKinney. The potentiometer was a Biddle high resistance instrument, accurate to 0.1 millivolt, used with an external galvanometer. The buret was 5 cc. in capacity and graduated to 0.02 cc. and was permanently connected to the source of alkali. All precaution was taken to exclude carbon dioxide. The solution was stirred with compressed tank nitrogen except when a volatile acid was titrated. In this case, the solution was stirred mechanically, or approximately nine-tenths of the alkali was added and the remainder of the titration carried out with nitrogen stirring. When using the agar-agar boundary, the reference solution was *n*-butyl alcohol saturated with respect to potassium chloride and benzoic acid. The solvent was *n*-butyl alcohol saturated with potassium chloride. The alkali was 0.05 *N* and was standardized potentiometrically against B. S. benzoic acid. It was prepared by dissolving c. p. stick potassium hydroxide in *n*-butyl alcohol and the insoluble carbonate removed by filtration. The quinhydrone was crystallized from *n*-butyl alcohol and melted sharply at 170° C.

Experiments

Known acids were dissolved in oil with subsequent determination of neutralization number in order to compare the results obtained employing four different procedures—namely, A. S. T. M. using methyl alcohol as a solvent, A. S. T. M. using ethyl alcohol as a solvent, alkali blue, and electrometric. The latter method was carried out with the two previously described reference electrodes (*5*, *6*). The concentration

[1] Received September 4, 1930.

of acids was chosen at random and in the case of the higher concentration of stearic acid in oil, a supersaturated solution was obtained. On long standing, stearic acid crystals separated and a more dilute solution was prepared. In each procedure, except the electrometric, the blank on the solvent was obtained by titration to a definite shade, and the solvent then added to the oil sample, whereupon the titration was carried out as near as possible to the same shade. In the case of the A. S. T. M. procedure using methyl alcohol, the point was difficult to obtain. A faint pink color is soon

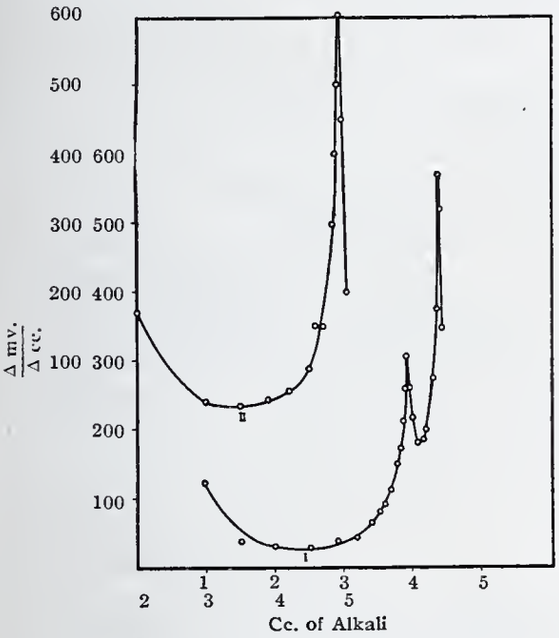


Figure 1—Electrometric Titration
I, Stearic acid; II, Abietic acid

obtained in the alcohol-water phase which does not appear to increase in depth until the end point recorded in the table was reached. Since the color change should be observed in the alcohol–water phase, care should be taken to allow the phases to separate even though working with an almost colorless oil. Table I is a tabulation of neutralization numbers obtained by titrating oil samples employing different methods.

Table I—Neutralization Numbers of Acids Dissolved in Transformer Oil

Method	Benzoic	Acetic	Stearic (I)	Stearic (II)	Cyclohexane Carboxylic	Rosin	Naphthenic Technical
CH_3OH, 50 cc. H_2O, 50 cc. Phenolphthalein (1%), 1 cc.	2.23	0.50	0.26	0.64	2.14	0.99	0.92
C_2H_5OH, 50 cc. H_2O, 50 cc. Phenolphthalein, 1 cc.	2.29	0.52	0.37	0.91	2.15	1.03	0.97
CH_3OH, 75 cc. Benzene, 75 cc. Alkali blue, 2 cc.	2.29	0.51	0.42	1.00	2.18	1.02	0.97
Water, 100 cc. Phenolphthalein, 1 cc.		0.47					
Electrometric[a] *n*-Butyl, 125 cc. Saturated KCl Quinhydrone, 0.05 gram	2.31	0.49	0.42	0.99	2.17	1.05	1.11

[a] Oil samples were rather concentrated. Experiments have been carried out whereby neutralization number was lowered to 0.1 by addition of neutral oil. Total oil sample then weighed 20 grams.

As may be seen from the table, serious differences may arise when such acids as stearic or abietic are present. In calculating the neutralization numbers, the strength of alkali was determined by titrating a weighed amount of benzoic acid using the four different methods when no oil was present. Table II contains the results of titrating stearic acid when no oil was present. Thus 0.005 gram of stearic acid was contained in one gram of oil sample (stearic acid II). A much larger amount was titrated in the absence of the oil and in Table II the number of the milligrams of potassium hydroxide equivalent to the 0.005 gram of stearic acid was calculated by proportion.

Table II—Titration of Stearic Acid in Absence of Oil

Method	Potassium Hydroxide Equivalent to 0.005 Gram Stearic Acid
	Mg.
CH_3OH and H_2O	0.95
C_2H_5OH and H_2O	0.95
CH_3OH and benzene	0.99
Electrometric	1.00

The discrepancies encountered with an acid of the stearic acid type practically disappear when the oil is absent. The difficulty is probably connected with the fact that two phases are present during the titration.

The results obtained when titrating stearic acid and rosin electrometrically were found to be approximately 10 per cent higher than expected. This suggested the possibility of an obscure peak in the electrometric titration curve when 90 per cent of the alkali was added. This possibility was verified in the case of stearic acid but not in the case of abietic acids, as Figure 1 shows.

Additional investigations have shown that a curve with two inflections was obtained in the titration of all of the acids. Furthermore, the relative position of the first point of inflection to the second point of inflection was due in part to the amount of quinhydrone present. Figure 2 shows the relative position of the two points of inflection in the titration of aliquot parts of the solvent when different amounts of quinhydrone were employed. However, there appears to be no stoichiometric relation between the amount of quinhydrone when calculated as a monobasic acid and the additional amount of alkali required. The experiment in which 0.01 gram of quinhydrone was used was repeated several times, and the result given represents an average value. A saturated solution was not employed due to the relatively large solubility of quinhydrone in butyl alcohol.

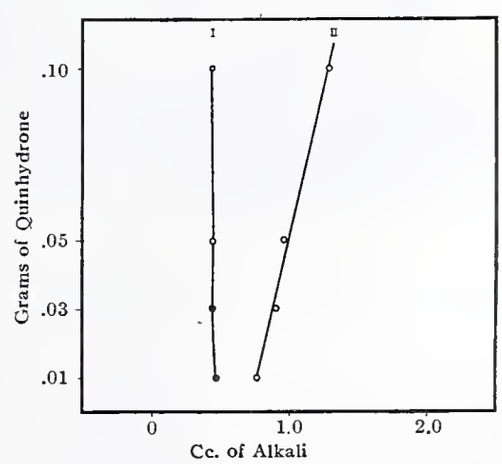


Figure 2—Relation of Amount of Quinhydrone to End Point of Titration
I, First point of inflection; II, Second point of inflection

It has been suggested that small amounts of oxygen in the compressed tank nitrogen may account for the second point of inflection. MacInnes and Jones (*3*) stirred their solutions mechanically in the presence of air and obtained two points of inflection which are attributed to quinhydrone as a weak acid. Rabinowitsch and Kargin (*4*) relate the phenomenon to the presence of carbon dioxide in the solution. Clarke and Wooten (*1*) failed to obtain two points of inflection in the absence of oxygen although these authors observed "marked irregularities on the alkaline side of the equivalence point." Our results are similar to those of MacInnes and Jones, although no attempt was made to eliminate the oxygen from the compressed tank nitrogen. It is probable that with

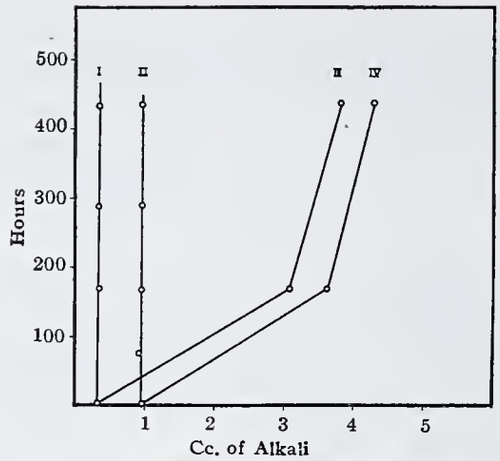


Figure 3—Relation of Time of Standing to Acidity of Solvent

I, First point of Inflection in dark; II, Second point of inflection in dark; III, First point of inflection in diffused daylight; IV, Second point of inflection in diffused daylight

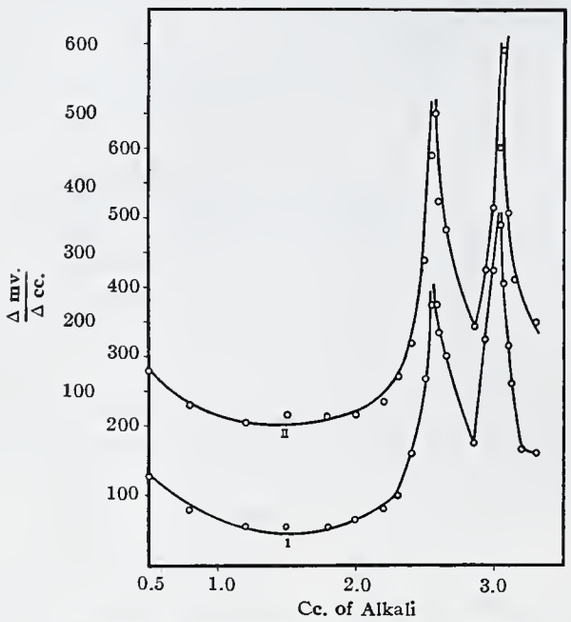


Figure 4—Electrometric Titration of Benzoic Acid

I, Silver–silver chloride electrode; II, Agar-agar boundary

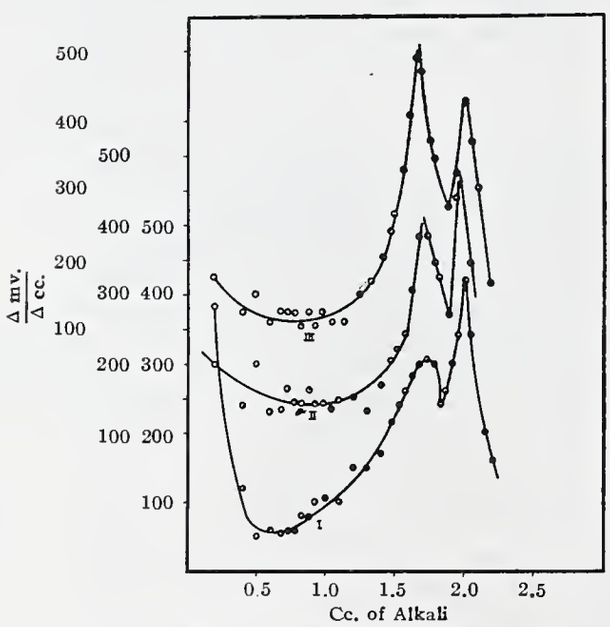


Figure 5—Electrometric Titration

I, Technicalabietic; II, Cyclo-hexane carboxylic acid; III, Benzoic

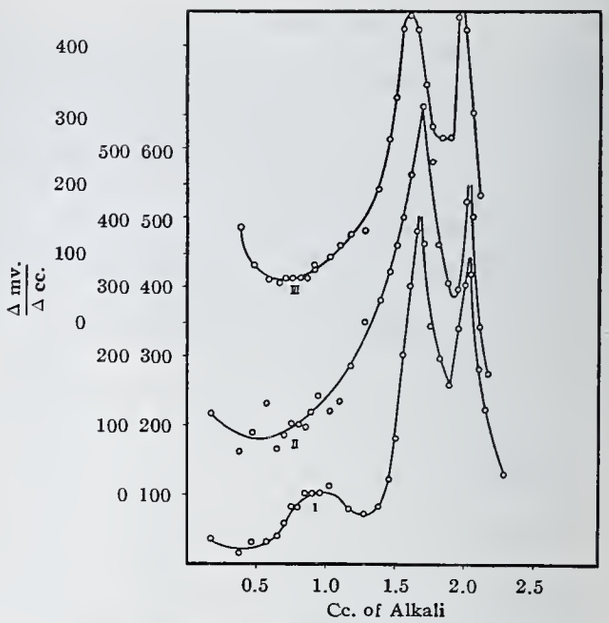


Figure 6—Electrometric Titration

I, Stearic; II, Salicylic; III, Technical naphthenic

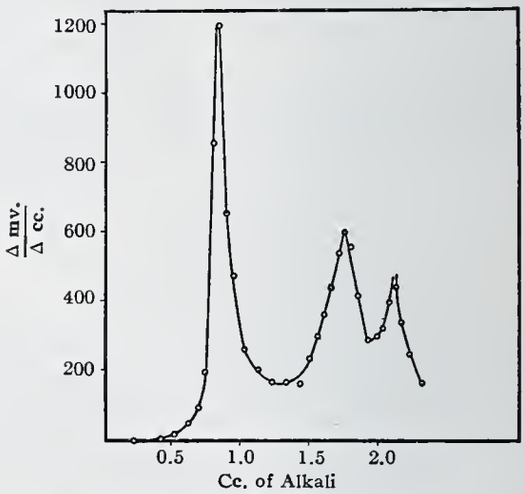


Figure 7—Electrometric Titration of Hydrochloric Acid in Butyl Alcohol

smaller amounts of quinhydrone than used in our experiments the two points of inflection would tend to merge and appear as one.

The variation in the acidity of the solvent was found to be mainly associated with the time of standing in the light, the time of reflux—i. e., in the preparation of the saturated solution—and the method used in dissolving the quinhydrone. Figure 3 represents the change in the acidity of the solvent when it was exposed to daylight and when it was stored in a dark bottle. If the saturated solution of potassium chloride in butyl alcohol is at an elevated temperature when the quinhydrone is added, the solution turns dark with an increase in the acidity of the solvent. A low and constant blank can be obtained by refluxing for $^1/_2$ hour, adding the quinhydrone when the solution is at room temperature, and storing the solution in a dark bottle.

The use of the silver–silver chloride electrode as a reference electrode (*6*) to replace the agar-agar boundary has been tried with success in this laboratory. A piece of silver sheet, 1-cm. square, was soldered with silver solder to a platinum wire 3 cm. in length. To the other end of the platinum wire, a piece of copper wire was soldered to serve as a lead to the potentiometer. A piece of glass tubing containing the copper wire was fused to the intervening platinum wire. The silver sheet was then covered with silver chloride by

merely dipping it into the fused salt. In this manner the time of preparation of the reference electrode is greatly reduced (*6*). The silver–silver chloride electrode was placed in the solution to be titrated together with the agar-agar electrode. The connections were changed after each addition of the alkali and the resulting points of inflection agreed very well. Apparently there is no diffusion of the benzoic acid from the reference electrode into the unknown acid sample when the agar-agar plug is correctly made (Figure 4). An off-balance of roughly 2 millivolts on the potentiometer can be observed when employing the agar-agar electrode whereas with the silver–silver chloride electrode, an off-balance of 0.5 millivolt is perceptible.

All the calculations in this paper are based on the first point of inflection which experimentally may be distinguished from the second by the color of the solution. In the former the solution is amber, whereas in the latter the solution is dark brown to black. If the first point of inflection is not obtained, the result is in error due to over-titration.

Additional electrometric titrations (Figures 5, 6, 7), employing the silver–silver chloride electrode as the reference electrode, were carried out in which known acid oil samples were added in equivalent amounts to the unknown acid in the solvent as calculated by the first point of inflection. In this manner two points of inflection were obtained in the experiment in which abietic acid was employed (Figure 5), whereas in Figure 1, employing five times as much abietic acid, only one point of inflection was obtained. Apparently, a preliminary titration is necessary in order to carry out satisfactorily an electrometric titration of an unknown oil sample. Three points of inflection were obtained when titrating hydrochloric acid. It is quite probable that the unknown acid in the solvent is not hydrochloric. Benzoic and salicylic acids behaved as a single acid. The question arises as to the use of the second point of inflection in the calculation of neutralization numbers. As applied to the acids used in these experiments, the authors prefer the first point of inflection from the standpoint of time consumed and of agreement of duplicate experiments. Obviously, dibasic acids and a mixture of acids of widely different strengths as well as the relative quantities of the acids present in the mixture have a bearing on the problem.

It is interesting to compare the order of the acids as determined by the potential of the cell at the halfway point of titration. The well-known relation between the ionization constant and the hydrogen-ion concentration in water at the halfway point of titration should enable one to arrange the acids in order of their strength. The solvent in our experiments was butyl alcohol, the single potential of the silver–silver chloride electrode in butyl alcohol is unknown, and the effect of the acid or acids in the solvent is unknown. However, the relative position of one acid to another should remain unchanged. The e. m. f. at the halfway point of titration when graphically obtained is approximate, since few points are ordinarily taken in that region of the curve. Table III contains these data.

Table III—Order of Acids as Determined by E. M. F. at Halfway Filtration Point

Acid	E. M. F. at Halfway Point	K_a in Water
Hydrochloric	340	
Salicylic	120	1×10^{-3}
Benzoic	65	6×10^{-5}
Cyclohexane carboxylic acid	40	
Technical naphthenic	40	
Stearic	25	
Abietic	20	

Literature Cited

(1) Clarke and Wooten, *J. Phys. Chem.*, **33**, 1468 (1929).
(2) Furman, Ind. Eng. Chem., Anal. Ed., **2**, 213 (1930).
(3) MacInnes and Jones, *J. Am. Chem. Soc.*, **48**, 2831 (1929).
(4) Rabinowitsch and Kargin, *Z. Elektrochem.*, **34**, 311 (1928).
(5) Seltz and McKinney, Ind. Eng. Chem., **20**, 542 (1928).
(6) Seltz and Silverman, *Ibid.*, Anal. Ed., **2**, 1 (1930).

Oxidation of Ferrous Iron by Iodine in Presence of Phosphate and Non-Existence of a Ferriphosphate Complex[1]

Walter D. Bonner and Hendrick Romeyn, Jr.

University of Utah, Salt Lake City, Utah

The reaction $Fe^{++} + {}^1/_2 I_2$ aq. $\longrightarrow Fe^{+++} + I^-$ goes to completion in the presence of phosphate and of a moderate concentration of acid. This reaction, even in solutions almost neutral, is too slow to be of analytical significance.

The reason for the completion of the reaction is probably the decrease in the ratio Fe^{+++} to Fe^{++} brought about by the addition of the phosphate.

Probably no complex ion is formed between ferric iron and phosphate, but only a weak electrolyte whose composition probably ranges from $FePO_4$ in solutions containing little phosphate, to $Fe(H_2PO_4)_3$ in solutions containing an excess of phosphate.

In 1926 Bonner and Yost (*1*) published a method for the determination of ferrous iron using sodium hypochlorite as the oxidizing agent. This method in brief is as follows: Ferrous iron, on being added to a solution containing disodium phosphate and sodium hypochlorite, is immediately oxidized to ferric iron and precipitated as a phosphate. Addition of iodide to this mixture results in the liberation of iodine and in the formation of a certain amount of iodate. Addition of acid dissolves the ferric phosphate, presumably with the formation of a complex ion (*7*). Any iodate present is at the same time reduced to iodine by the iodide. The liberated iodine is then titrated with thiosulfate. The reactions involved are:

$$2Fe^{++} + ClO^- + 2H^+ \longrightarrow 2Fe^{+++} + Cl^- + H_2O \quad (1)$$
$$3I^- + 4ClO^- + 2H^+ \longrightarrow IO_3^- + 4Cl^- + H_2O \quad (2)$$

The fundamental idea on which this method is based is that the ferric iron, converted by the phosphate into a fairly stable complex, is thus removed from the scene of the reaction. There will therefore be no reverse reaction of ferric iron with iodide, which ordinarily prevents the titration of

[1] Received June 9, 1930.

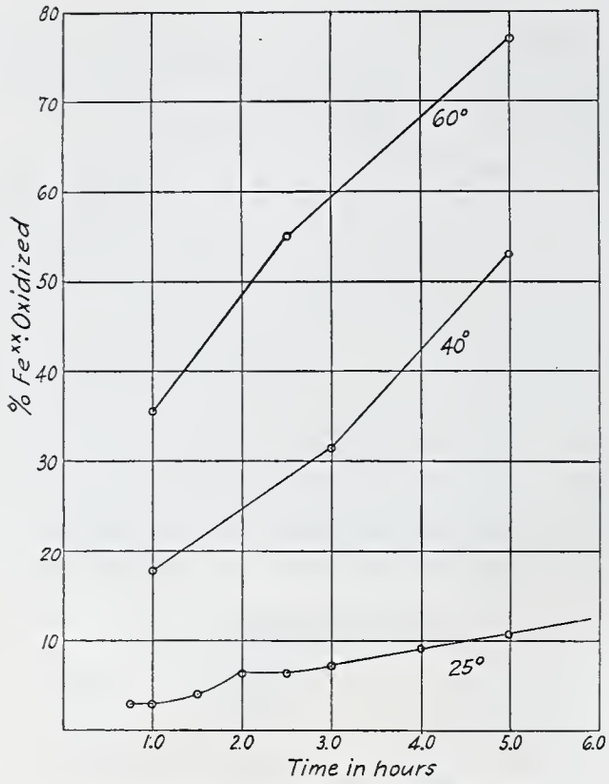


Figure 1—Rate of Oxidation of Iron by Iodine

ferrous iron with iodine. The idea of the complex was based upon the work of Wineland and Ensgraber (*7*) already referred to.

H. W. Foote (*3*) has suggested that the above method be further simplified, either by direct titration of the ferrous iron by iodine in the presence of phosphate, or by adding an excess of iodine solution also in the presence of phosphate, and titrating back with thiosulfate. That these proposed modifications were not practicable was known to Bonner and Yost at the time they wrote their paper. Nevertheless, acting on Foote's suggestion, we have made a more careful examination of the reactions involved.

Rate of Oxidation of Iron by Iodine

We first determined the rate of the oxidation of ferrous iron by iodine in the presence of phosphate, the solutions being 0.1 *N* in sulfuric acid. In this way we were able to show that the reaction actually goes to completion. The procedure adopted was to mix together, in glass-stoppered flasks, 15 cc. of 0.1 *N* ferrous sulfate solution; 15 cc. of 0.3 *N* disodium phosphate solution; 25 cc. of 0.1 *N* iodine solution; 50 cc. of water. The mixed solutions were always 0.1 *N* in sulfuric acid which was added with the ferrous sulfate solution. These flasks were kept in a thermostat at the desired temperature. At definite intervals a flask was removed and the excess iodine titrated with thiosulfate. A large number of these determinations was made, and the results are readily reproducible. Figure 1 shows that the reaction is very slow at 25° C., being in fact less than 50 per cent complete in 24 hours. At 40° C. the reaction is complete in about 15 hours, and at 60° C. in about 9 hours. We have no explanation for the curious hump in the 25° C. curve.

The data on which the curves of Figure 1 are based are given in detail in Table I. Each titration given is the mean of at least two determinations. The precision of the experiments at 40° and 60° C. is of course much less than that of experiments at 25° C. due to the higher vapor pressure of the iodine causing some loss from the solutions.

Willard and Hall (*6*) have shown that small amounts of ferrous iron in the presence of phosphate and in solutions approximately neutral are almost immediately oxidized by iodine. Therefore we also determined the rate of the reaction at various other acid concentrations. Using aurine indicator to obtain neutral solution, as suggested by Willard and Hall, we made rate measurements at 25° C. on solutions of pH approximately 6.5, 2.5, and 1.5. At pH 6.5, and using solutions about 0.03 *N* in ferrous iron, the reaction is complete in about 6.5 hours. At pH 2.5 about 75 per cent of the iron has been oxidized in 18 hours. At pH 1.5, the rate is about the same as at pH 1.0, where most of our measurements were made.

Table I—Rate of Oxidation of Iron by Iodine

25° C.; Thiosulfate Equivalent, 23.70 cc.			40° C.; Thiosulfate Equivalent, 24.1 cc.			60° C.; Thiosulfate Equivalent, 24.1 cc.		
Time	Thio-sulfate	Fe^{++} Oxi-dized	Time	Thio-sulfate	Fe^{++} Oxi-dized	Time	Thio-sulfate	Fe^{++} Oxi-dized
Hours	*Cc.*	*%*	*Hours*	*Cc.*	*%*	*Hours*	*Cc.*	*%*
0.00	37.45	0.00	0.00	33.65	0.0	0.0	33.65	0.0
0.75	36.81	2.74	1.00	29.3 ± 0.3	17.8	1.0	25.1 ± 0.1	35.5
1.00	36.80	2.74	3.00	26.0 ± 0.2	31.5	2.5	20.3 ± 0.3	55.0
1.50	36.47	4.13	5.00	20.8 ± 0.2	53.1	5.0	15.1 ± 0.3	77.0
2.00	35.89	6.60						
2.50	35.95	6.34						
3.00	35.76	7.11						
4.00	25.28	9.14						
5.00	34.90	10.78						
20.50	30.01	31.40						
24.00	29.12	35.18						

Using only 5 mg. of ferrous iron, we were able to corroborate the statement of Willard and Hall, referred to above. It is interesting to note that we were able to carry out this oxidation in the absence of phosphate, the ferric iron in this case being precipitated as the hydroxide instead of as a phosphate. In the absence of phosphate, however, the results were erratic and usually low. These neutral solutions either with or without phosphate are very sensitive to atmospheric oxidation, and air must be rigorously excluded.

Theoretical Considerations

Since this reaction goes actually though slowly to completion, and if the formation of a ferriphosphate complex might be assumed, the explanation seems almost obvious. The two reactions whose rates are involved are evidently:

$$Fe^{+++} + H_2PO_4^- \longrightarrow \text{complex} \qquad (3)$$
$$Fe^{++} + \tfrac{1}{2} I_2 \text{ aq.} \longrightarrow Fe^{+++} + I^- \qquad (4)$$

Reaction 3 must be rapid, as is evidenced by the work of Bonner and Yost (*1*). Reaction 4 is probably rather slow and the equilibrium is known to be established quite slowly.

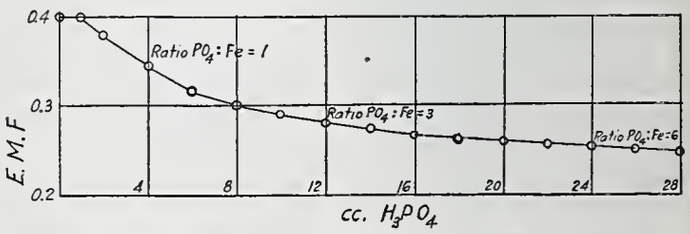


Figure 2—Potentiometric Titration of Ferric-Ferrous Solution with Phosphoric Acid

At equilibrium and in the absence of phosphate, only a small part of the iron has been oxidized. The reason that Reaction 4 goes to completion as written must be that the concentration ratio Fe^{+++} to Fe^{++} in the presence of phosphate and a low H^+ concentration is smaller than the equilibrium ratio of Fe^{+++} to Fe^{++} in the same reaction, phosphate being absent. This latter equilibrium ratio is readily determined, and is known to be approximately 10^{-3} (*2*). In order to show what

the ratio Fe^{+++} to Fe^{++} is in a solution containing phosphate, the following experiments were performed:

A solution was made up containing 25 cc. of 0.05 *M* ferrous sulfate solution, 0.5 cc. of 0.05 *M* ferric sulfate solution, 0.5 cc. of 0.1 *N* sulfuric acid solution, and 25 cc. of water. The ratio Fe^{+++} to Fe^{++} in this solution was 0.02 or $10^{-1.70}$. The measured e. m. f. of this solution at 25° C. against a normal calomel electrode was 0.359 volt. An entirely similar solution was then made up, excepting only that the 25 cc. of water were replaced by 25 cc. of a 0.3 molal solution of disodium phosphate. This solution gave an e. m. f. against the same calomel electrode at 25° C. of 0.255 volt. From these measurements, by means of the relationship

$$E = E_o + 0.059 \log Fe^{+++}/Fe^{++}$$

we calculate that the ratio Fe^{+++} to Fe^{++} is now $10^{-3.45}$. The addition of the phosphate has therefore greatly decreased the concentration of Fe^{+++} in the solution, and has decreased the ratio Fe^{+++} to Fe^{++} to a value markedly less than the equilibrium ratio of Reaction 4. This seems to substantiate our previous statement that the reason this reaction goes to completion must be the decreased ratio Fe^{+++} to Fe^{++}. This may be brought about by the formation of a ferriphosphate complex. This conclusion is made the more plausible by the fact that while the reaction is completed in solutions 0.1 *N* in sulfuric acid, the reaction is not completed in solutions approximately 3 *N* in acid. In other words, at acid concentrations such that this hypothetical complex cannot form, equilibrium is established with but little Fe^{+++} present. If one carries out this oxidation in solutions nearly neutral, the progress of the reaction is accompanied by the formation of a white precipitate, presumably a ferric phosphate. This precipitate, filtered out and washed, dissolves slowly in 3 *N* sulfuric acid to a colorless solution. Addition of iodide to this solution liberates, at once, an abundance of iodine, showing that at such an acid concentration, the reaction cannot go to completion.

Non-Existence of Ferriphosphate Complex

The fact that the oxidation of ferrous iron by iodine fails to proceed in the presence of 3 *N* acid seems to indicate that any complex which may be formed is not a very stable one. The evidence for the existence of such a complex seems to be furnished entirely by the work of Wineland and Ensgraber (*7*) who assign to it the formula $Fe(PO_4)_2^{---}$. If any complex is formed, even of moderate stability, it should be possible to determine both its presence and its composition by means of a potentiometric titration of a ferric-ferrous solution with phosphoric acid (*4*). Such a titration has been carried out and its graph is given in Figure 2. For purposes of comparison, the graphs obtained by titrating (*a*) silver nitrate with potassium cyanide and (*b*) silver nitrate with ammonia, Figure 3, are inserted. As is readily seen, the iron-phosphate graph shows no indication of any complex as stable as the silver ammonia complex. From coördination considerations, the most likely complexes should be $Fe(HPO_4)_3^{---}$ or $Fe(H_2PO_4)_6^{---}$. No indication is given of either of these. The existence of any ferriphosphate complex must, therefore, be called in question and the behavior of ferric solutions containing phosphate attributed to the formation of a weak electrolyte. Since, as the graph shows, the rapid change in the Fe^{+++} to Fe^{++} ratio has ceased when the ratio of phosphate to ferric iron has become about 3, we may conclude that the ultimate composition of the weak electrolyte approximates $Fe(H_2PO_4)_3$. However, the addition of a small amount of phosphoric acid removes most of the color from a ferric solution. Thus, in the titrations just cited, the greater part of the color disappeared with the addition of the first cubic centimeter of phosphoric acid. Ten cubic centimeters of 0.1 *N* ferric chloride solution are almost completely decolorized by 0.5 cc. of 85 per cent phosphoric acid. These observations suggest that some compound richer in iron than is the primary phosphate is present in the solutions which contain little phosphoric acid. In the second case cited, the ratio of phosphate to iron is 1, suggesting the formula $FePO_4$.

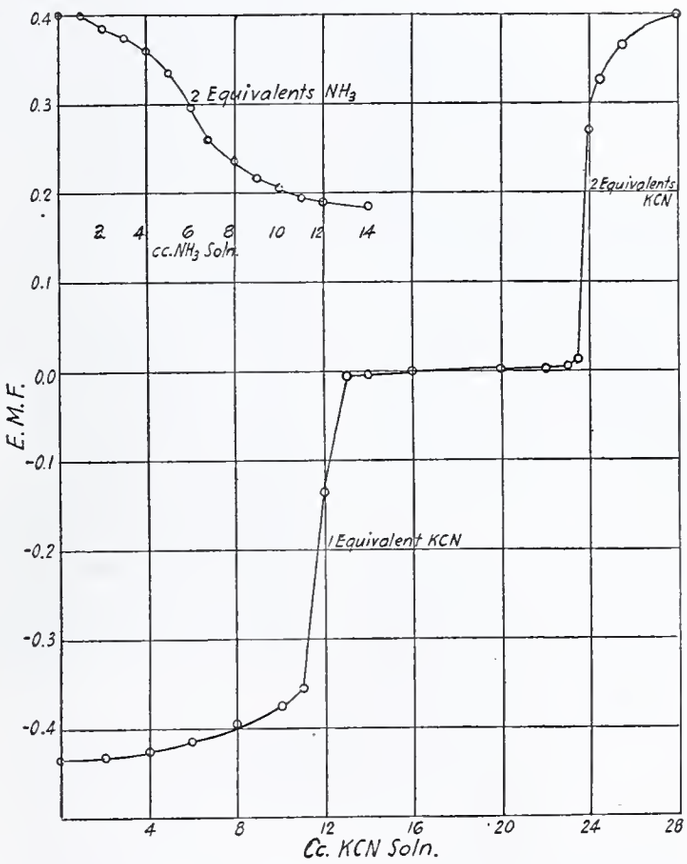


Figure 3—Titration of Silver Nitrate

The white precipitate referred to above, which forms during the oxidation of ferrous iron by iodine in nearly neutral solutions containing phosphate, contains as an average of 4 analyses, 26.8 per cent iron. These analyses were made by the method of permanganate titration, following reduction with stannous chloride (*5*). Similar analyses made of the product called by Wineland and Ensgraber "alkali free ferriphosphoric acid" gave 26.6 per cent iron. As the compound $Fe_2(HPO_4)_3$ contains 28.0 per cent iron, it is probable that each of these substances is the secondary ferric phosphate.

Acknowledgment

A part of this work has been done by the senior author in the Gates Chemical Laboratory of the California Institute of Technology. He wishes here to express his appreciation of all the many courtesies shown him.

Literature Cited

(1) Bonner and Yost, Ind. Eng. Chem., **18**, 55 (1926).
(2) Fales, "Inorganic Quantitative Analysis," p. 291, Century, 1925.
(3) Foote, "Annual Survey of American Chemistry," Vol. 2, p. 134 (1927).
(4) Kolthoff and Furman, "Potentiometric Titrations," p. 99, Wiley, 1925.
(5) Treadwell-Hall, "Analytical Chemistry," pp. 11 and 609, Wiley, 1919.
(6) Willard and Hall, *J. Am. Chem. Soc.*, **44**, 2244 (1922).
(7) Wineland and Ensgraber, *Z. anorg. Chem.*, **84**, 340 (1913).

Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid[1]

Hobert H. Willard and R. C. Gibson

Department of Chemistry, University of Michigan, Ann Arbor, Mich.

Chromium and vanadium may be completely oxidized to chromic and vanadic acid by boiling 70 per cent perchloric acid, the oxidizing action of which is removed by dilution with water, after which any of the usual titration methods may be used. Manganese is not oxidized.

Directions are given for applying this process to the analysis of chromic oxide, chromite, steel, and ferrochromium.

If phosphoric acid is added, manganese is oxidized more or less completely to a manganic salt, but the oxidation of chromium is hindered.

Small amounts of tungsten do not interfere but larger amounts must be removed before oxidation and may be subsequently added to the solution as sodium tungstate.

If both phosphotungstic acid and vanadium are present, low results are obtained.

Chromium may be precipitated as lead chromate from a solution 1 molar in perchloric acid and 0.04 molar in lead perchlorate and thus separated from vanadium, manganese, and iron.

Most of the present volumetric methods for the determination of chromium depend upon its oxidation to chromic acid by an excess of oxidizing agent, removal of the latter, and titration with a suitable reducing agent. The removal of this excess of oxidizing agent and the effect of manganese are more or less troublesome. This paper describes a more rapid method for chromium in which the presence of manganese does not interfere.

About ten years ago one of the authors (*11*) reported that hot, concentrated perchloric acid would oxidize chromic oxide and its salts, and applied it to steel analysis, but the high price of the acid made its extensive use impracticable. The acid is now relatively inexpensive, and it seemed desirable, therefore, to study the method in detail so that it might find the wide use which its convenience and accuracy would seem to warrant. Up to the time this paper was presented (*1*), no further reference to this subject had appeared. Since that time Lichtin (*6*) has suggested the use of perchloric acid in the analysis of chrome alum and its liquors. He erroneously assumed that chloric acid was an intermediate product in the oxidation process. James (*3*) has given brief directions for its use in the analysis of chromium iron alloys. No analyses, however, were given to show the accuracy of his procedures, some of which are known to be inaccurate.

Perchloric acid, like sulfuric, in dilute solution is very stable and not affected by any of the ordinary reducing agents. Upon boiling it loses water until it reaches a concentration of 70 to 72 per cent, and this acid distils at about 203° C., accompanied by some decomposition, thus:

$$4HCl_4 = 2Cl_2 + 7O_2 + 2H_2O$$

Oxides of chlorine are not formed.

This oxygen is available for oxidation and under these conditions the acid is a powerful oxidizing agent. To remove its oxidizing power, all that is required is dilution with water. The free chlorine present is readily removed by boiling or blowing air through the solution. Nearly all metals and non-metals are readily attacked by the hot, concentrated acid. Manganese, however, is not oxidized beyond the bivalent state except when considerable phosphoric acid is present. In this respect it differs from other oxidizing agents for chromium. Even chromite and chromic oxide, which are quite inert towards other acids, are completely oxidized. The method is very rapid. Moreover, since concentrated perchloric acid is an excellent dehydrating agent for silica (*12*), the latter may be determined after titration of the chromium with no extra trouble. It is not, however, satisfactory for removing tungstic acid (*12*).

In spite of the properties mentioned above, 70 to 72 per cent perchloric acid is perfectly stable and non-oxidizing at ordinary temperatures, but obviously should be kept out of contact with organic matter. It is non-explosive and no trouble has been experienced with violent reactions, even when used by students.

Commercial perchloric acid, free from ammonium, chromium, and vanadium, is entirely satisfactory for the determination of the latter elements and is much cheaper than the C. P. acid.

Standardization of Dichromate

C. P. potassium dichromate, unless specially purified, is not a safe primary standard. It may even contain a slight excess of chromic acid. The material used in this work was the best obtainable, but it was tested in two ways—against U. S. Bureau of Standards arsenious oxide, which gave a value of 100.06 per cent dichromate, and against ferrous sulfate which had been titrated against permanganate standardized against Bureau of Standards sodium oxalate, which gave 100.16 per cent. The arsenite method (*9*) was more accurate because only one titration was involved and because dilution and acidity were without effect. The dichromate must not be added to the alkaline arsenite solution or too much arsenite will be used. One gram of dried potassium dichromate was dissolved in 25 cc. of water and acidified with 6 to 8 cc. of sulfuric acid (sp. gr. 1.5). To this solution was added 1.02 grams of dried arsenious oxide dissolved in 25 cc. of water and 3 grams of sodium hydroxide crystals. Reduction of dichromate was complete in a minute or two. Fifty cubic centimeters of hydrochloric acid (sp. gr. 1.1) were added and the excess arsenite titrated with 0.02 *N* bromate which had been standardized against arsenious oxide using approximately the same concentration of hydrochloric acid. Change in acidity, volume of solution, and concentration of substances have a negligible effect on the ratio of arsenite to dichromate, but a certain minimum concentration of hydrochloric acid must be present in the bromate titration, the end point of which may be determined electrometrically (*17*) or by the use of methyl orange indicator, if the color of the solution is not too deep. The excess of arsenite may also be titrated with permanga-

[1] Received November 10, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minn., September 9 to 13, 1929.

nate, using a trace of iodine as catalyst, with or without erioglaucine A as indicator (*5*).

Standardization of Ferrous Sulfate

It has been shown by Eppley and Vosburgh (*1*) that the result of a dichromate–ferrous sulfate titration is influenced by acidity, volume of solution, and concentration of dichromate. Their results show variations of more than 0.5 per cent when these factors are varied. The following experiments confirm their results: In solutions 3.4 molar with respect to sulfuric acid, 25 cc. of 0.1 *N* dichromate in a volume of 150 cc. required 25.43 cc. of ferrous sulfate when titrated electrometrically, and when the volume was doubled, 25.35 cc. Portions of 50 cc. with the same acidity required, in volumes of 100 cc. and 600 cc., 51.96 cc. and 50.66 cc., respectively, of another ferrous sulfate solution. The presence of ferric or perchlorate ion has no effect on the location of the end point. It is obvious, therefore, that it is essential to standardize the ferrous sulfate under the same conditions of acidity and volume prevailing in the analysis, using, preferably, about the same amount of titrating solution.

If it is desired to use diphenylbenzidine as indicator (*15*), the acidity must be reduced by the addition of sodium acetate sufficient to react with all free sulfuric or perchloric acid. This was shown by titrating 25-cc. portions of 0.1 *N* dichromate under different conditions. In all cases the solution had a volume of 150 cc. and contained 15 cc. of phosphoric acid (sp. gr. 1.37). In one case it was titrated directly, using diphenylbenzidine as indicator, and required 25.51 cc. of ferrous sulfate. In two parallel experiments the solution contained 20 cc. of 70 per cent perchloric acid, was treated with 32 grams of sodium acetate trihydrate, and the value, 25.41 cc., was obtained both electrometrically and by the indicator method.

To work out the conditions necessary to obtain satisfactory chromium determinations, synthetic mixtures of iron and chromium were prepared using ingot iron and the tested potassium dichromate. The oxidation was carried out in a beaker 20 cm. in height and of 350 cc. capacity. This extra-tall beaker, ordinarily unnecessary, was used to avoid any possible loss, either by spraying from the gases evolved or from the occasional bumping of the dilute perchloric acid. The concentrated acid boils quietly.

Amount of Perchloric Acid Required—If too little acid was used, solid ferric perchlorate separated even in the boiling acid and the results were low. For 1 gram of iron, 20 cc. of 70 per cent acid were satisfactory, for 2 grams, 25 cc., and for 5 grams, 60 cc. Less is likely to cause incomplete oxidation of chromium, especially if the sample is dissolved directly in the hot acid, some of which is thus used up.

Time of Boiling for Complete Oxidation—The oxidation is the critical part of the process. After the acid has concentrated to dense fumes, 20 minutes of gentle boiling is sufficient, unless some reducing material, such as carbon, is present. Oxidation starts rather suddenly and the change in color due to the formation of red chromic acid is usually quite evident. Ten or fifteen minutes more is sufficient to complete the oxidation. The beaker must be kept covered, and should be at least 11 or 12 cm. high, the 500-cc. tall form with lip being satisfactory. A Soxhlet flask of this capacity is still better and prevents any possibility of mechanical loss by bumping or spraying. A conical flask is not so good because the depth of liquid is not great enough. Most of the acid condenses and runs down in oily drops on the sides of the vessel and on the cover glass. This appearance is an excellent sign that the acid is sufficiently concentrated to have its maximum oxidizing power. Much time is saved by dissolving the sample directly in the concentrated acid, if possible, taking care not to heat too strongly at first. When the solution must be evaporated to fumes, especial care is needed to prevent mechanical loss.

If the concentrated acid solution is allowed to stand overnight before titration, some oxygen is apparently lost and results are slightly low.

Time of Boiling to Remove Chlorine—Three minutes was found sufficient. The solution must, of course, first be diluted to at least double its volume. The chlorine may also be removed by bubbling air through the solution.

Interference of Ammonium Salts—Slightly low results were always obtained in the presence of ammonium salts. The error amounted to about 1 mg. of chromium in 50 mg. when 1 gram of ammonium nitrate was added. It is therefore important that when commercial perchloric acid is used, it be free from ammonium salts.

Action of Other Substances—Halides, nitrate, and acetate are volatilized. Sulfate in moderate amount does not interfere except that most sulfates are insoluble in perchloric acid and cause bumping. Reducing agents in general and even graphitic carbon are entirely oxidized in a short time. Vanadium is completely oxidized to vanadic acid. Tungsten in large amounts is incompletely oxidized by perchloric acid, and if already oxidized to tungstic acid, carries down appreciable amounts of chromium and vanadium. Phosphate in considerable amount, as will be shown later, tends to prevent complete oxidation of chromium unless the quantity of perchloric acid is greatly increased.

The results shown in Table I were obtained by the following procedure: The requisite amounts of ingot iron and potassium dichromate were weighed into a tall, 400-cc. lipped beaker. Five cubic centimeters of water and 1 cc. of nitric acid were added, and enough hydroxylamine hydrochloride to reduce the chromium. At least 25 cc. of 70 per cent perchloric acid were added, followed by the desired amount of ingot iron. The solution was boiled until the appearance of dense white fumes of perchloric acid and for 15 to 20 minutes longer to complete the oxidation. An equal volume of water was added to the somewhat cooled solution, which was boiled to expel chlorine, diluted, cooled, and titrated electrometrically with ferrous sulfate standardized at the time it was used, against dichromate under the same conditions of volume and acidity.

Table I—Determination of Chromium and Vanadium in Synthetic Mixtures of Iron and Chromium after Oxidation with Perchloric Acid

Weight of Sample	Chromium Added	Chromium Found
Grams	%	%
5	0.274	0.273
5	0.264	0.263
2	0.708	0.707
2	0.666	0.664
1.5	0.879	0.876
1.5	1.020	1.020
0.4	14.23	14.21
0.4	14.48	14.48
0.35	77.47	77.43
0.35	76.53	76.52

Procedure for Chromium and Vanadium Steels Containing Little or No Tungsten

Place samples of 0.5 to 2 grams, depending on the chromium content, in a 500-cc. tall-form lipped beaker, or better still in a 500-cc. Soxhlet flask, and add 20 to 25 cc. (depending on the size of the sample) of 70 per cent perchloric acid, commercial or c. p. Cover the vessel and warm until all the metal has dissolved, taking care not to let the action become too violent. Most steels will dissolve in less than 5 minutes. Boil the solution 15 to 20 minutes, noting the change in color if much chromium is present, and continuing the boiling at least 10 minutes longer. The perchloric acid, should condense and run down the sides of the beaker or flask. Cool somewhat, add an equal volume of water, and boil 3 minutes to expel chlorine. After cooling, the solution

is diluted to a suitable volume and is ready for titration as described later.

Cast iron or alloys high in carbon should be dissolved in dilute perchloric acid, either with or without nitric acid, and evaporated to fumes; the action of the hot concentrated acid is too violent. If it is necessary to use 4- or 5-gram samples, add 50 or 60 cc. of acid. This is desirable in cast iron or steel very low in chromium. Boiling for 1 or 2 hours may be necessary to oxidize all the graphite, and further addition of perchloric acid may become necessary.

Procedure for Ferrochromium

An alloy of this type requires different treatment, because when boiled with 70 per cent perchloric acid, the chromium trioxide formed, which is fairly insoluble even in the hot acid, tends to coat the particles of ferrochromium and prevent further oxidation. Weigh 0.2 gram of the powdered alloy into a 500-cc. tall lipped beaker or Soxhlet flask. Add 20 cc. of hydrochloric acid, sp. gr. 1.18, and heat for 15 minutes. Add 15 cc. of 70 per cent perchloric acid and boil 30 minutes after all hydrochloric acid is expelled. Cool somewhat, add a few cubic centimeters of water to dissolve the chromium trioxide, and reoxidize by boiling 15 minutes after the water is expelled. Add a few cubic centimeters of water and look for any undissolved particles of metal. If any are present, another oxidation may dissolve them. Otherwise pour off most of the solution, add a few cubic centimeters of 70 per cent perchloric acid to the residue, and boil till solution is complete. Add the main decanted liquid, evaporate off the water, and reoxidize for 5 minutes. Dilute and boil off chlorine.

Table II shows the results obtained with steels and ferrochromium.

Table II—Determination of Chromium and Vanadium in Steel and Ferrochromium after Oxidation with Perchloric Acid

Wt. of Sample	Chromium Present	Chromium Found $FeSO_4$ indicator	Chromium Found $FeSO_4$ electrometric	Arsenite Permanganate (5)	Vanadium Present	Vanadium Found (5)
Grams	%	%	%		%	%
		Cast Iron, B. S. 82				
5	0.24	0.240	0.240			
5	0.24	0.239	0.240			
5	0.24	0.240				
		Cr-Ni Steel, B. S. 32b				
2	0.638	0.637	0.637			
2	0.638	0.636	0.638			
		Cr-Mo Steel, B. S. 72				
1.5	0.911	0.908	0.909			
1.5	0.911	0.910	0.909			
		Stainless Steel, B. S. 73				
0.4	13.93	13.89	13.90	13.88		
0.4	13.93	13.92	13.89	13.88		
0.4	13.93	13.92	13.91			
		Ferrochromium, B. S. 64				
0.15	67.9	67.80	67.78			
	67.9	67.79	67.81			
		Cr-V Steel, B. S. 30a				
2.0	1.02			1.005	0.21	0.21
2.0	1.02			1.010	0.21	0.21
2.0	1.02			1.010	0.21	0.21

Procedure for Chromic Oxide and Chromite

Chromic oxide, which is not attacked by the usual acids, is readily oxidized to chromic acid by boiling 70 per cent perchloric acid, a 0.15-gram sample requiring 15 minutes. Chromite is more resistant; if ground to pass a 200-mesh sieve it requires 60–90 minutes. Storer (*7*, *10*) suggested the use of concentrated nitric acid and sodium chlorate for this purpose. Gröger (*2*) used it successfully for chromic oxide, but both he and others found that it did not completely dissolve chromite.

Pure chromic oxide was prepared by precipitating mercurous chromate from chromic acid solution and igniting it in hydrogen.

Weigh a 0.5-gram sample into a tall, 500-cc. lipped beaker, or better still, Soxhlet flask. Add 20 cc. of 70 per cent perchloric acid and boil 30 to 60 minutes. Cool somewhat, then add a few cubic centimeters of water to dissolve the chromium trioxide which coats the particles. If any unattacked ore remains, evaporate off the water and boil the concentrated acid again for 20 or 30 minutes. If this treatment does not decompose all the ore, pour off most of the solution, add to the residue 10 cc. of perchloric acid, and boil until the ore is dissolved. Add the main decanted solution, evaporate off the water, oxidize 5 minutes, dilute, and boil off the chlorine. The solution is diluted to a suitable volume and when cool, is ready for titration.

The results obtained by this procedure, using samples of chromite and pure chromic oxide, are shown in Table III.

Table III—Determination of Chromium in Chromic Oxide and Chromite after Oxidation with Perchloric Acid

Chromic Oxide Present		Chromic Oxide Found (Electrometric)
Gram		*Gram*
	CHROMIC OXIDE	
0.1423		0.1424
0.1401		0.1401
0.1409		0.1408
0.1423		0.1422
0.1471		0.1471
	CHROMITE	
%		%
57.49[a]		57.48
57.49		57.47

[a] Decomposed by perchloric acid, oxidized by persulfate.

Titration of Chromic Acid

After the chromium has been oxidized as already described, it may be titrated by any of the usual methods.

(1) Excess of standard ferrous sulfate is added and the excess is titrated back by means of standard permanganate, allowing 1 minute for the end point if vanadium is present. This method is so well known as to need no description. The color due to ferric perchlorate is so slight that there is no advantage in adding phosphoric acid. In the absence of vanadium, the end point is made much sharper by adding 0.5 cc. of a 0.1 per cent solution of erioglaucine A, better known as alphazurine (Schultz 506) as recommended by Knop (*4*). The change from green to red after the addition of an excess of 0.03 cc. of 0.1 *N* permanganate in 300 cc. is very distinct even in the presence of the chromic salt. The color lasts only a few seconds.

(2) Excess of standard arsenite is added, which is then back-titrated with permanganate in the presence of hydrochloric acid and a trace of iodide as catalyst, as described by Kolthoff and Sandell (*5*). If vanadium is absent, alphazurine as indicator improves the end point. In testing this method 2-gram samples were used, phosphoric acid was not really necessary, and vanadium was determined in the same solution by titration with ferrous sulfate using diphenylbenzidine as indicator, following the directions of the authors. Good results were obtained. The amount of acetate to be added is discussed in connection with the next method.

(3) The chromic acid (and vanadic acid, too, if present) is titrated directly with standard ferrous sulfate either electrometrically in a strongly acid solution, or by the use of diphenylbenzidine as indicator in a solution containing phosphoric acid and sufficient sodium acetate to react with all the perchloric acid present, according to the method of Willard and Young (*15*). The procedure is as follows: After boiling off the chlorine, cool, dilute the perchloric acid solution to 200 to 400 cc., add 15 cc. of phosphoric acid (sp. gr. 1.37) and, stirring constantly, a weight of sodium acetate trihydrate equivalent to the excess of perchloric acid used in dissolving the steel. One gram of iron was found to require about 5.4 cc. of 70 per cent perchloric acid

for conversion into ferric perchlorate, and 1 cc. of this acid contains 1.17 grams of perchloric acid, equivalent to 1.58 grams of crystallized sodium acetate. Thus, if 20 cc. of acid are added, the excess will require about 23 grams of acetate. If the steel was first dissolved in nitric acid, the excess of perchloric acid will be a little greater. The proper amount of acetate has been added when more would form a permanent white precipitate of ferric phosphate. If this occurs, add dilute sulfuric acid, with constant stirring, until the solution clears. Unless the acidity is reduced in this way, the color change at the end point will be slow. Add 0.6 to 0.8 cc. of 0.1 per cent diphenylbenzidine solution (in phosphoric or acetic acid), and allow 5 minutes, but not more than 10, for the purple color to develop. It will appear brownish until most of the chromic acid is reduced. If no color appears, add a few drops of dilute sulfuric acid. Titrate with ferrous sulfate to a clear green, approaching the end point carefully. Add a correction of 0.04 cc. of 0.1 *N* ferrous sulfate for each 0.5 cc. of indicator.

For the electrometric method add 25 to 30 cc. of sulfuric acid (sp. gr. 1.5) and titrate chromic plus vanadic acids with ferrous sulfate. If much vanadium is present, a much sharper end point is obtained by cooling the solution to 5° C.

Whichever method is used, it has already been shown that the ferrous sulfate should be standardized in the same way and under the same conditions of volume and acidity at about the time it is used.

Titration of Vanadium

This may be determined by any of the usual methods, a list of which is given in references (*15*) and (*5*).

Silica has been dehydrated by the boiling perchloric acid and after the titration it may be filtered off and determined (*12*).

These different methods were used in obtaining the concordant results shown in Table II.

Steels Containing Tungsten

When present in considerable amount, tungsten is only slowly and incompletely oxidized by hot 70 per cent perchloric acid. The tungstic acid formed seems to protect some of the metal. Dilute acid dissolves the steel, leaving tungsten powder, which is incompletely oxidized by the concentrated acid. The steel was, therefore, dissolved in hydrochloric acid, the tungsten oxidized by boiling with nitric acid in the usual way, and the solution evaporated with 25 cc. of 70 per cent perchloric acid. The concentrated acid was boiled 20 minutes to oxidize the chromium which was titrated with ferrous sulfate. The steel contained 4.10 per cent chromium, 14.80 per cent tungsten, and no vanadium. The amount of chromium found was about 1 mg. too low.

The precipitate of tungstic acid was filtered off and dissolved in hot, dilute sodium hydroxide. It contained about 1 mg. of chromium, mostly as chromate, and accounted completely for the low results. The chromic acid is noticeably adsorbed by it. The precipitate takes on a deeper orange color. This effect was further shown by mixing sodium tungstate and chromate solutions, adding perchloric acid, evaporating, and boiling. The amount of chromium in the precipitate was always 1 or 2 mg. When vanadium was present, about the same proportion of it was found in the tungstic acid. Several days' leaching of the precipitate with dilute sulfuric acid failed to remove any of these metals. Moreover, the amount of ferric oxide in the precipitate was much greater. One-gram samples of Bureau of Standards Steel 50 containing 17.56 per cent tungsten, 3.61 per cent chromium, and 0.76 per cent vanadium, were treated as above. The precipitate of tungstic acid contained 6.4 mg. of iron, 1.4 mg. of chromium, and 0.3 mg. of vanadium as oxides. When corrected for these impurities, 17.63 per cent of tungsten was obtained. In a steel containing 5.8 per cent of tungsten it was difficult to obtain a clear filtrate, but even with cinchonine the value obtained was only 5.60 per cent. The procedure recommended by James (*3*) is, therefore, unsatisfactory. All the silica was contained in these precipitates.

It seemed worth while to try to prevent the interference of tungsten by converting it into the soluble phosphotungstic acid. Certain difficulties were encountered, however. Phosphoric acid tends to prevent complete oxidation of chromium by perchloric acid, as shown in Table IV. Dichromate was added and reduced by hydroxylamine hydrochloride. Each result is the average of two or more experiments.

Table IV—Effect of Phosphoric Acid on Oxidation of Chromium by Perchloric Acid

Eighty-five Per Cent Phosphoric Acid	Seventy Per Cent Perchloric Acid	Time of Oxidation	Chromium Present	Error Chromium
Cc.	*Cc.*	*Minutes*	*Mg.*	*Mg.*
5	20	15	100	−4
5	20	30	100	−7
15	20	15	100	−40
15	20	30	100	−50
5	25	20	50	−1.3
5	30	20	50	−1.0
5	35	20	50	−0.8
5	25	20	25	−0.5
5	32	25	25	−0.3
5	40	25	25	−0.3
5	30	25	25	−0.2
5	35	25	25	−0.1

Effect of Manganese

It is well known that trivalent manganese is stabilized by phosphoric acid. It was found that by boiling the correct mixture of perchloric and phosphoric acids, manganese could be quantitatively oxidized to a manganic salt and titrated by ferrous sulfate. If, therefore, chromium is oxidized in the presence of considerable phosphoric acid as described above, the manganic salt must be reduced before the chromic acid is titrated, and dilute hydrochloric acid is suitable for this purpose. One-gram samples of steel to which manganese sulfate was added were boiled 25 minutes with 3 cc. of 85 per cent phosphoric acid and 35 cc. of 70 per cent perchloric acid. The solutions were diluted to 150 cc., the stated amounts of 2.3 *N* hydrochloric acid (one part of concentrated acid and four of water) added, and after boiling 5 minutes any manganic salt present was titrated electrometrically with ferrous sulfate. The results are shown in Table V.

Table V—Effect of Hydrochloric Acid (2.3 *N*) on Manganic Phosphate

Manganese Present	Manganese Found after Addition of HCl					
	0	1 cc.	2 cc.	3 cc.	5 cc.	10 cc.
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
11.3	5.1	3.3	1.0	0	0	0
51	18.0				0.3	0
101	40.6					0.2

In all cases there was insufficient phosphoric acid for complete oxidation. Ten cubic centimeters of 2.3 *N* hydrochloric acid are sufficient to reduce considerable amounts of manganese, and it was found that it would not reduce any of the chromium when 50 mg. of it and 2 grams of iron were present. Even 25 cc. caused only a slight reduction.

These results show that if even 5 cc. of 85 per cent phosphoric acid are present, the amount of perchloric acid must be greatly increased even with small amounts of chromium, and that with larger amounts, even this does not entirely eliminate the error.

It was found that 10 cc. of 85 per cent phosphoric acid were required to keep in solution 0.2 gram of tungsten when boiled with 30 cc. of perchloric acid. With 5 cc., a heavy cream-colored precipitate formed which persisted on dilution, but this amount of phosphoric acid was sufficient for 0.1 gram of tungsten, the slight precipitate dissolving on dilution.

Three cubic centimeters were sufficient for 0.05 gram. In the presence of 1 and 2 grams of iron, however, 5 cc. are sufficient for 0.1 and 0.15 gram of tungsten, respectively. Using 3 cc. of phosphoric acid under the same conditions, a precipitate forms but dissolves when 10 cc. more are added after dilution, and the solution boiled. Table VI shows the results obtained by oxidizing chromium under varying conditions, using in all cases 3 cc. of 85 per cent phosphoric acid and 35 cc. of 70 per cent perchloric acid. After dilution, 10 cc. more of the former were added. Each of the errors shown is the average of several experiments.

Table VI—Effect of Phosphotungstic Acid on Oxidation of Chromium by Perchloric Acid

Iron	Tungsten	Chromium	Error Chromium
Grams	*Grams*	*Mg.*	*Mg.*
1	0.1	12	−0.07
1	0.1	50	−0.20
1	0.2	50	−0.25
2	0.2	50	−0.07
0.75	0.2	50	−0.35
2[a]	0.2	50	+0.03

[a] No phosphoric acid added after oxidation. Solution cleared on dilution.

By using the conditions of the last experiment in Table VI, adding extra iron, dissolving the steel in a mixture of phosphoric, nitric, and hydrochloric acids, and reducing the manganic salt by hydrochloric acid, the right value was obtained for a steel containing 18.7 per cent tungsten and 3.13 per cent chromium. In another experiment using the conditions of the next to the last analysis in Table VI, the result was 3.08 per cent. This error of 0.5 mg. of chromium persisted in all cases where 10 cc. of phosphoric and of dilute hydrochloric acid were added after the oxidation, and was probably due to some reducing material in the acid. One gram of steel containing 15 per cent of tungsten required no extra phosphoric acid to keep it in solution.

Effect of Vanadium

If vanadium is present, low results for chromium are always obtained, so that the above method is of somewhat limited applicability. In the presence of phosphotungstic acid, Willard and Young (*15*) have shown that vanadic acid forms a complex which is only partially reduced by ferrous sulfate. Attempts to break up this complex by boiling with perchloric acid or by adding fluoride were without effect.

To show the magnitude of this error, varying amounts of vanadium as sodium vanadate were added to 1 gram of a steel containing 4.10 per cent chromium, which was treated as described above for chrome-tungsten steel. Assuming that all the chromium was titrated, the errors in vanadium, with 2, 10, and 30 mg. of the latter present, and 0.2 gram of tungsten, were −1.7, −3.9, and −5.0 mg., respectively. With 0.1 gram of tungsten, the corresponding errors were −1.5, −2.1, and −3.6 mg. of vanadium.

Method Not Involving Phosphoric Acid

Willard and Young (*15*) have shown that a large amount of tungstic acid, as sodium tungstate, may be added without precipitation to an acid solution containing sufficient ferric salt. This dissolved tungstic acid does not interfere in the electrometric titration of chromic and vanadic acids. In applying this to a chrome-vanadium-tungsten steel, from which tungsten had been removed in the usual way and the chromium and vanadium in the filtrate oxidized by perchloric acid, it was noticed that if the tungstic acid was dissolved off the filter by hot 4 per cent sodium hydroxide and added to the oxidized filtrate containing sufficient iron, the results were always low by 0.5 mg. of chromium, even if the tungstate solution had been oxidized by peroxide or persulfate. This was proved to be due to organic matter introduced by the filter paper, no matter whether the sodium hydroxide was hot, cold, or fairly dilute. Sodium carbonate solution did not cause this error but it was impossible to oxidize all the chromium in the residue. It seemed essential, therefore, to fuse the tungstic oxide with sodium carbonate, the air acting as oxidizing agent. Although more troublesome, this method has been shown to eliminate all errors.

Procedure for Chromium or Chromium and Vanadium in Tungsten Steels

A sample of 1 to 1.5 gram is usually convenient. Place it in a 150- or 250-cc. beaker, and add 10 cc. of water and 30 cc. of hydrochloric acid (sp. gr. 1.18). Heat until the steel is completely decomposed and to the hot solution add cautiously from a pipet 8 to 10 cc. of nitric acid (sp. gr. 1.42), without removing the cover glass. Boil gently with occasional swirling until all dark metallic particles have been oxidized to yellow tungstic acid, and evaporate to 20 cc. If necessary, add 10 cc. of hydrochloric acid and 3 cc. of nitric, and boil down again to 20 cc. Dilute to 75 cc., boil a few minutes to dissolve all salts, filter into a 500-cc. Soxhlet flask, or, less satisfactorily, into a tall 500-cc. lipped beaker, and wash with hot, 2 per cent hydrochloric acid. Remove the flask or beaker and wash out the acid with 1 per cent ammonium nitrate solution, taking care that these washings are discarded because ammonium salts prevent complete oxidation of chromium.

To the filtrate add 1 gram of iron as ferric chloride or nitrate, but not sulfate; if a 1.5-gram sample was used, add only 0.5 gram of iron. Add 25 cc. of 70 per cent perchloric acid (or more if a larger sample was taken) and evaporate to fumes of the acid.

In the meantime, ignite the tungstic acid precipitate in an open platinum or iron crucible and fuse it for 5 minutes with 1.5 grams of sodium carbonate with free access of air. Or fuse with sodium peroxide in an iron crucible free from chromium, dissolve in water, and boil to remove peroxide.

Boil the main perchloric acid solution in the covered flask or beaker 20 minutes after the appearance of dense fumes of the acid. Dilute with an equal volume of water, boil 3 minutes to expel chlorine, and while still hot, pour into it with constant stirring the sodium tungstate solution together with the small amount of ferric oxide which it contains. A clear solution will result.

Determination of Chromium

If only chromium is to be determined, add to the cool solution excess of standard ferrous sulfate and titrate back with permanganate as previously described. No phosphoric acid is needed. The arsenite method of Kolthoff and Sandell may also be used. The ferrous sulfate must be standardized under the same conditions of acidity and volume.

Determination of Vanadium

Vanadium may be determined in the same solution after destroying the excess of permanganate by a drop of arsenite (*5*), but the vanadic acid must be titrated electrometrically with ferrous sulfate, because, as has already been pointed out, tungsten prevents the formation of color with diphenylbenzidine.

The excess of permanganate may be conveniently destroyed by adding 1 or 2 cc. of 0.1 *M* sodium azide (*16*) and boiling for a moment, or at room temperature by adding more azide and letting stand a short time.

Boiling with a little dilute hydrochloric acid is also effective.

Determination of Chromium and Vanadium

To the perchloric acid solution, add 25 cc. of sulfuric acid (sp. gr. 1.5), cool, and titrate chromic and vanadic acids

electrometrically with ferrous sulfate. If much vanadium is present, cool the solution to 5° C.

The tungstic acid in solution begins to precipitate after several hours.

Indicator Method for Chromium and Vanadium

This differs from the method just described in the removal of tungstic acid to prevent its interference with the indicator. Proceed as already described including the filtration and washing of the tungstic acid precipitate. Use paper pulp. The oxidation of chromium in the filtrate is carried out in the same way, except that no iron is added, and the titration is carried out as directed. If no color develops, it is probable that tungstic acid was not completely removed or too much acetate was added.

The small amounts of chromium and vanadium in the tungstic acid are determined colorimetrically after fusion in an open crucible with 1 or 2 grams of sodium carbonate (*15*). The melt is dissolved in water and filtered. If it is colorless, no chromium is present. If it is yellow, estimate the chromium by matching the color in a beaker with an alkaline solution of equal volume to which standard dichromate is added. Then acidify the solution with phosphoric acid and estimate the vanadium colorimetrically by the method of Willard and Young. If chromium is present, add to the vanadium standard an equivalent amount of dichromate.

One-gram samples of Bureau of Standards Steel 50 containing 17.56 per cent tungsten, 3.61 per cent chromium, and 0.756 per cent vanadium, were treated as described, the chromium being titrated by the ferrous sulfate–permanganate method, without any indicator. The values obtained were 3.61, 3.61, 3.60, 3.62, and 3.60 per cent. In the first experiment, 10 cc. of 85 per cent phosphoric acid were added before the permanganate titration, but the end point was sharper without it. The value for vanadium in one sample was found to be 0.753 per cent by adding 20 cc. of 0.1 *M* sodium azide to reduce the excess of permanganate, letting stand 20 minutes at room temperature, and titrating vanadic acid electrometrically with ferrous sulfate.

It should be noted that perchloric acid is an excellent solvent for many alloys which dissolve with difficulty in other acids.

Separation of Chromium as Lead Chromate from Perchloric Acid Solution

It has been shown by Willard and Kassner (*8*, *14*) that lead chromate is completely insoluble in 1 *M* perchloric acid which is 0.01 *M* in lead perchlorate, and practically insoluble in 5 *M* acid if twice as much lead is present. It would thus appear quite feasible to separate chromium from vanadium, manganese, and other metals by precipitation as lead chromate after oxidation by perchloric acid as described above. The results of experiments along this line showed that such a method was possible if proper conditions were maintained.

Lead perchlorate was prepared by evaporating lead nitrate with a slight excess of perchloric acid as described by Willard and Kassner (*13*), but no attempt was made to free it from acid. A salt prepared from litharge seemed to contain some reducing material. The solution was diluted to 0.5 molar.

Lead chromate was completely precipitated in a short time from a solution containing considerable iron, 1 *M* perchloric acid and 0.04 *M* lead perchlorate. These were adopted as standard conditions. Such a solution contains in 200 cc., 16 cc. of 0.5 *M* lead solution and 17 cc. of 70 per cent perchloric acid. Extra lead must be added if much chromium is precipitated, 100 mg. of chromium requiring 4 cc. of 0.5 *M* solution.

A solution oxidized by boiling perchloric acid always contains, after dilution, small amounts of chloride which interfere slightly with complete precipitation of lead chromate. The addition of a few drops of silver perchlorate, prepared from the nitrate in the same way as the lead salt, removed this source of error. It was sometimes necessary to neutralize part of the free acid, and ammonia was found best for this purpose because sodium hydroxide usually contains chloride and sometimes reducing substances. The procedure followed, after the perchloric acid solution had been boiled to remove chlorine, was to neutralize part of the acid if necessary, add a slight excess of silver perchlorate, heat just to boiling, add the proper amount of lead perchlorate, and cool to room temperature, stirring occasionally. If filtered hot, some chromate remained in solution. The precipitate was very dense and crystalline. It was filtered on a Gooch crucible, washed with cold water, transferred to a beaker, excess of standard arsenite added, then 50 cc. of hydrochloric acid (sp. gr. 1.09), after which the excess of arsenite was titrated with bromate. The lead chromate could also be dissolved in saturated sodium chloride solution containing 1 cc. of concentrated hydrochloric acid per 100 cc., and titrated with ferrous sulfate. If 1 gram of the steel is dissolved in 20 cc. of 70 per cent perchloric acid and diluted to 175 or 200 cc., the acidity will be about right.

Good results were obtained when about 80 mg. of chromium were present, but with 30 mg. there was an error of −0.2 to 0.3 mg., the cause of which is yet unexplained. Vanadium was determined in the filtrate by titration with ferrous perchlorate to avoid precipitation of lead sulfate, and the results were good when all the chromium had been precipitated. In a solution containing tungstic acid held in solution by ferric perchlorate, 0.6 to 0.8 mg. of chromium remained in solution. Further work is in progress to obviate the difficulties mentioned. Table VII shows the results obtained under proper conditions.

Table VII—Separation of Chromium as Lead Chromate

Weight of Sample	Chromium Present	Chromium Found	Vanadium Present	Vanadium Found
Grams	%	%	*Mg.*	*Mg.*
		Cr-Ni Steel, B. S. 32b		
2.2	0.638	0.635		
2.2	0.638	0.630		
		Stainless Steel, B. S. 73		
0.6	13.93	13.89		
0.6	13.93	13.88		
		Synthetic Mixture		
Grams Fe	*Mg.*	*Mg.*		
3	83.15	83.15	32.7	32.5
3	83.55	83.60	32.7	32.5

Manganese can be determined in the filtrate from lead chromate by methods not applicable in presence of chromium.

Literature Cited

(1) Eppley and Vosburgh, *J. Am. Chem. Soc.*, **44**, 2148 (1922).
(2) Gröger, *Z. anorg. Chem.*, **81**, 233 (1913).
(3) James, *Chemist-Analyst*, **19**, No. **5**, 14 (1930).
(4) Knop, *Z. anal. Chem.*, **77**, 125 (1929).
(5) Kolthoff and Sandell, Ind. Eng. Chem., Anal. Ed., **2**, 140 (1930).
(6) Lichtin, *Ibid.*, **2**, 126 (1930).
(7) Pearson, *Am. J. Sci.*, II, **48**, 198 (1869).
(8) Seidell, "Solubility of Inorganic and Organic Substances," p. 1258, Van Nostrand, Supplement 1928.
(9) Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1911).
(10) Storer, *Proc. Am. Acad. Arts Sci.*, 4, 338 (1860); *Am. J. Sci.*, II, **48**, 190 (1869).
(11) Willard and Cake, J. Ind. Eng. Chem., **11**, 480 (1919).
(12) Willard and Cake, *J. Am. Chem. Soc.*, **42**, 2208 (1920).
(13) Willard and Kassner, *Ibid.*, **52**, 2391 (1930).
(14) Willard and Kassner, *Ibid.*, **52**, 2402 (1930).
(15) Willard and Young, Ind. Eng. Chem., **20**, 764, 769 (1928).
(16) Willard and Young, *J. Am. Chem. Soc.*, **51**, 139 (1929).
(17) Zintl and Wattenberg, *Ber.*, **56**, 472 (1922).

Determination of pH of Ammonia Latex[1]

J. McGavack and J. S. Rumbold

General Laboratories, United States Rubber Company, Passaic, N. J.

The pH of latex has been determined at various concentrations of ammonia (1) by the use of indicators, and (2) by the application of the glass electrode. The two curves thus obtained were comparable but not identical.

It is shown that the glass electrode gives results reproducible with a high degree of accuracy up to pH 9.5 and a fair degree of accuracy up to pH 11.0. Above pH 11.0 it is necessary to calibrate each electrode. An ordinary galvanometer allowed measurement of the e. m. f. to 1 millivolt. The assymetry of the glass was so small as to be negligible.

THIS paper covers the work done so far in these laboratories on the development of an accurate and rapid method for determining the pH of latex.

From a practical viewpoint one of the most troublesome features of the direct use of a hydrogen electrode is the deposition of a film of rubber on the platinum, which by increasing the internal resistance of the cell, so reduces the sensitivity of the null point instrument that after a few determinations the apparatus must become inoperative. A more serious objection to this electrode is the uncertainty attached to measurements made in solutions containing proteins.

The glass electrode, however, is believed to be very satisfactory. Although no comprehensive theory of its mechanism has yet been formulated, it has been used successfully under conditions where the hydrogen electrode and indicators would be useless (*4, 3*). In this paper a method of making and using a modified Haber cell is described, and the results of measurements of the pH values of normal latexes are compared with those previously obtained by means of indicators.

Colorimetric Method

The successful use of indicators depends upon the preparation of a clear serum. This was done by mixing about 50 cc. of latex with 0.5 gram of carbon black, then filtering 20 cc. of the mixture under a pressure of 15 lbs./sq. in. (1.0563 kg./sq. cm.). Probably by causing a partial coagulation of the rubber particles the carbon black increased the rate of filtration without appreciably altering the pH of the serum, though even under the most favorable circumstances not more than 2 or 3 cc. of serum could be obtained in an hour. The filter was made by pouring a mixture of Cellite and water on a filter paper in a small Buchner funnel, washing it with water several times by suction, and finally drying it at 100° C. The funnel was closed with a rubber stopper kept tight by two metal plates bolted together, and air-pressure was applied through a tube in the stopper. It was necessary to use pressure instead of suction to minimize loss of ammonia by vaporization, but the ammonia content of the filtrate was always less than would be expected when calculated from the results of titration of the latex on the assumption that all the ammonia is in the serum. The difference could be partly accounted for by adsorption of ammonia on the carbon black, but it is no doubt also due to adsorption of ammonia on the rubber particles.

The example of data given in Table I obtained by titration of latex and the serum prepared from it by pressure filtration shows that this use of carbon black in pH measurement might be expected to give low results. That no corresponding difference of pH was found may be ascribed to the inadequacy of the colorimetric method to measure small changes of hydrogen-ion activity.

[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

The pH of the serum was determined by the familiar comparator method, about 2 cc. being required for each determination. It is claimed that an accuracy of about ±0.1 can be obtained by means of indicators, but when they are used with latex serum a more liberal allowance for error must be made.

Most of the available indicators for use in alkaline solution are unsatisfactory on account of their small color change, and the presence of proteins in the solution under examination is known frequently to cause large error. That the measurements were sometimes unreliable was proved when two indicators covering the same pH range did not agree even approximately, and a partial discharge of the color of the indicator often occurred, probably because of adsorption on colloidal matter. Owing to the difficulty in obtaining reliable results it was decided that an electrometric method must be used. The experimental results obtained with indicators and latex serum are shown graphically in Figure 1.

Table I—Titration of Latex and Serum by Pressure Filtration
(33.1% solids)

NH_3 in Latex	Calcd. NH_3 in Serum	Obsd. NH_3 No carbon black	Obsd. NH_3 Carbon black
%	%	%	%
1.46	2.18	1.93	1.75
2.18	3.26	2.70	2.53

The Glass Electrode

MacInnes and Dole (*6*) who have recently studied the effect of variation in the composition of the glass on its suitability as an electrode, recommend a soda-lime glass of composition disilicon oxide, 72 per cent; calcium oxide, 6 per cent; and sodium oxide, 22 per cent (Number 015, supplied by the Corning Glass Company, Corning, N. Y.). This glass has been used to make bulbs for the electrodes in the following way: Electrodes 1, 2, and 3 were made by drawing out at one end a tube of soft laboratory glass, diameter 13 mm., to a diameter about 5 mm. A piece of the special glass was fused in the narrow end of this tube and blown into the form of a small bulb, strong enough to withstand the pressure of 2 or 3 inches (5.08 or 7.62 cm.) of 0.1 *N* hydrochloric acid, yet so thin that the resistance was surprisingly low and screening was unnecessary. An ordinary Leeds and Northrup galvanometer was sensitive enough to allow measurement of the e. m. f. within 1 millivolt, which corresponds to an accuracy of about ±0.02 pH. The open end of the tube was coated with paraffin, then filled with 0.1 *N* hydrochloric acid, and closed by a rubber stopper to prevent evaporation when not in use. Figure 2 shows the wiring of the arrangement with a diagrammatic representation of the glass electrode and the calomel half cell. Instead of having the rest of the electrode within the bulb it was combined with a 0.1 *N* hydrochloric acid calomel electrode, the side tube of which was lowered into the acid in the bulb when a measurement of e. m. f. was to be made.

It was thought that as this bulb might consist partly of glass from the supporting tube it would be unsatisfactory, and the bulbs of electrodes 1-A, 2-A, 3-A, 4-A, and 5-A were blown from tubes of the special glass. However, the data given below show that except in strongly alkaline solution, electrode 3 is in good agreement with the others.

Calibration of Electrodes—Sorensen's glycine sodium chloride-sodium hydroxide standards were used (pH values at 25° C. obtained by slight interpolation of those given by Clark, *1*).

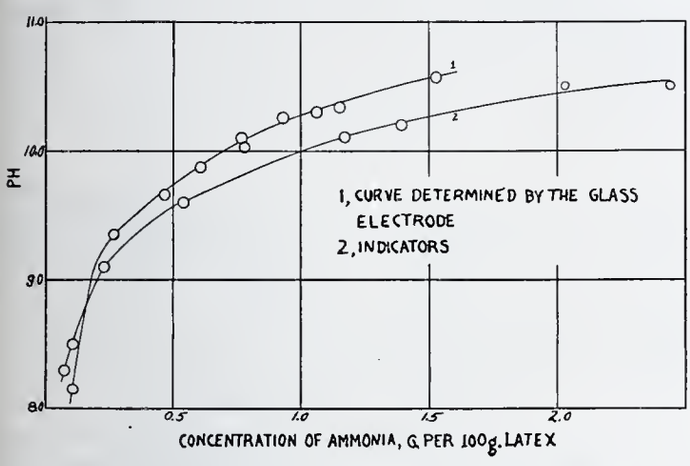


Figure 1—Relation between Concentration of Ammonia and pH

Materials—Fifty per cent sodium hydroxide solution allowed to stand in a Pyrex tube till the carbonate settled. Portion of clear solution diluted with boiled distilled water and adjusted to 0.1 *N*. Stored in a paraffined Pyrex bottle.

Thirty-six per cent hydrochloric acid solution diluted and adjusted to 0.1 *N* with anhydrous sodium carbonate.

Potassium chloride, sodium chloride, and glycine. Best obtainable materials recrystallized several times.

All rubber stoppers were boiled in sodium hydroxide solution, hydrochloric acid, then water.

Buffer standards of pH greater than 11 kept in paraffined Pyrex bottles.

The slide wire, *S* (maximum scale reading 1000), used as a potentiometer, was proved to have a uniform resistance, and the voltmeter was calibrated with a standard Weston cell. The slide wire setting was varied to give voltmeter readings at intervals of 0.1 volt, and assuming a uniform voltage drop in the slide wire, the actual voltage was calculated in each case from the reading of the null point for the Weston cell. To determine the e. m. f. of the glass electrode cell the null point was first obtained, and then the slide wire was set to show a voltage of 0.5, corresponding to an actual voltage of 0.5810 when corrected by the calibration curve of the voltmeter. The e. m. f. was calculated from the readings of the slide wire at the null point and at 0.5810 volt.

By the use of the resistance box, *R*, the e. m. f. range could be varied.

Table II—E. M. F. of Cell with Buffer Standards

(Electrode 3)

pH of Buffer Standard (Soln. *X*)	Slide Wire Reading at Null Point[a]	E. M. F. of Cell
		Volt
8.43	561	0.3812
8.77	593	0.4030
9.54	681	0.4628
10.30	751	0.5103
11.12	814	0.5531
11.89	876	0.5953
12.45	915	0.6218
12.74	931	0.6325

[a] Slide wire reading at 0.581 volt 855 throughout.

Calculation of E. M. F.—The arrangement is:

Hg | HgCl, KCl (satd.) ‖soln. *X* | glass | 0.1 *N* HCl, HgCl | Hg

Assuming the glass surface reversible to the hydrogen-ion activity, this combination will be equal in potential to the sum of the two cells.

(A) Hg | HgCl, KCl (satd.) ‖soln. *X* | H_2
(B) Hg | HgCl, 0.1 *N* HCl | H_2

The potential of (A) at 25° C. is

$$E = 0.2458 + 0.05915\ pH_x \quad (2)$$

and of (B), 0.3989 (*5*). The relation between the e. m. f. and the pH of solution *X* is, therefore, at 25° C.:

$$E = -0.1531 + 0.05915\ pH_x$$

Table III—Comparison of Observed with Calculated Values of E. M. F. of Cell 1

(Electrode 3)

pH of Soln. *X*	E Theoretical	E Observed	Deviation
			Millivolts
8.43	0.3455	0.3812	35.7
8.77	0.3656	0.4030	37.4
9.54	0.4112	0.4628	51.6
10.30	0.4561	0.5103	54.2
11.12	0.5064	0.5531	46.7
11.89	0.5502	0.5953	45.1
12.45	0.5833	0.6218	38.5
12.74	0.6004	0.6325	32.1

The values given in Table III are not shown graphically but were used to obtain the curve in Figure 1.

Determination of pH of Normal Latex—The results given in Table IV were obtained with latex *X*-167 (total solids 37.9 per cent, ammonia 0.84 per cent). The ammonia content was varied by adding small quantities of a 24 per cent aqueous solution of ammonia to about 500 cc. of latex, and it was determined in each case by titrating against 0.1 *N* hydrochloric acid 1 or 2 grams diluted with water to 300 cc.

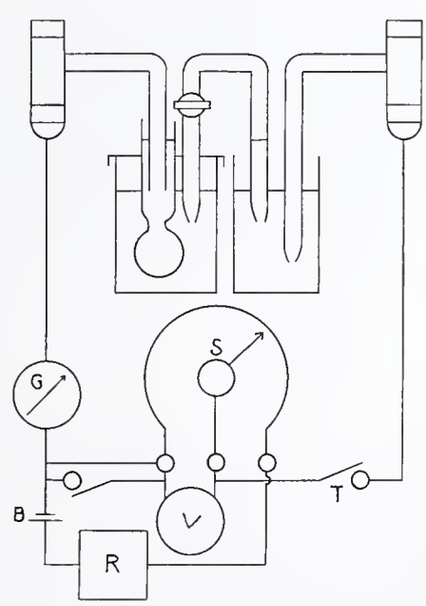


Figure 2—Wiring of Cell and Potentiometer

These results are plotted as a smooth curve in Figure 1. It will be noticed that the "blown" latex returned to very nearly the same pH when ammonia was added to it, showing that the removal of ammonia is probably a reversible process.

It was impossible to prevent the deposition of a film of rubber on the glass bulb. This did not seem to affect the e. m. f., but it greatly reduced the sensitivity of the galvanome-

ter. The bulb was, therefore, washed in ammonia solution, and the rubber film could be removed by means of a small brush. Since it was necessary to clean the electrode in this way after each determination, the Haber form is better than the more fragile type devised by MacInnes and Dole (a very thin membrane sealed on the end of a supporting tube).

Table IV—pH of Latex *X*-167
(Electrode 3)

NH_3 per 100 Grams of Latex	Slide Wire Reading at Null Point[a]	E. M. F.	pH from Calibration Curve
Gram			
	LATEX BLOWN AND STIRRED FOR 2 HOURS		
0.11	524	0.356	8.15[b]
0.27	660	0.448	9.35
0.47	691	0.470	9.66
0.61	711	0.483	9.87
0.77	731	0.497	10.10
	LATEX AS RECEIVED		
0.78	725	0.493	10.03
0.93	746	0.507	10.26
1.06	751	0.510	10.30
1.15	753	0.512	10.34
1.53	771	0.524	10.57

[a] Slide wire reading at 0.581 volt 855.
[b] pH value obtained by extrapolation.

The reversibility of the electrode after use with latex was checked against some of the original buffers. The results of this test appear in Table V.

Table V—Stability of Electrode 3

pH of Buffer Standard	E. M. F. of Cell after Use with Latex	Previous E. M. F.	Change
			Millivolts
9.54	0.4600	0.4628	− 2.8
10.30	0.5096	0.5103	− 0.7
11.12	0.5402	0.5531	−12.9
11.89	0.5953	0.5953	0

It was known that the standard of pH 11.12 had probably changed, and neglecting the result with this solution the reversibility of the electrode is apparently fairly satisfactory.

Reproducibility of Electrodes

Owing to the rather fragile nature of the glass electrodes it is desirable that as well as being reversible they should be readily reproducible. The reproducibility has been examined over the pH range 8.4 to 12.7. The calibration curves of a few electrodes (Figure 3) show that up to about pH 9.5 the variation is negligible. Even at pH 11.0 the greatest difference is still small, but in strongly alkaline solution the variations between electrodes which agree at lower pH may be large.

For accurate work above pH 9.5 it is therefore necessary to determine the calibration curve of each electrode, but a fair degree of accuracy, without recalibration, can be expected up to about pH 11.0.

It is, however, very necessary to know the composition of the solution under examination. The lowest curve obtained with glycine–sodium hydroxide buffer standards with a small constant concentration of sodium chloride is remarkably different, and the divergence begins at a lower pH.

Owing to this depression of the e. m. f. of the glass electrode by sodium chloride it would be better to use gylcine–sodium hydroxide buffer mixtures for calibration instead of Sorensen's standards, but as the effect is large only at high pH, and Sorensen's standards of greatest alkalinity have only a small concentration of this salt, the error introduced by their use is probably small. It would be best to calibrate the electrodes with glycine–sodium hydroxide mixtures for the pH range 8.0 to 11.0, and with sodium hydroxide solutions of known pH for values above 11.0.

It is the experience of the authors that up to pH 10.0 or 11.0 most of the electrodes differed only slightly and there is little difficulty in obtaining reliable results, but beyond pH 11.0 careful calibration of the electrode immediately before use is essential.

It is also necessary to allow the electrodes to reach equilibrium. Immediately after filling them with acid the e. m. f. is always high, and an equilibrium value is reached in about 24 hours; the bulbs were therefore filled with acid and immersed in water for a day or two before they were used.

Asymmetry Potential of the Glass

The potential in the glass bulb of electrode 3 was measured by combining it with a 0.1 *N* hydrochloric acid calomel electrode, both immersed in a 0.1 *N* solution of the hydrochloric acid. The asymmetry potential of the glass indicated by the e. m. f. of this cell was so small as to be negligible.

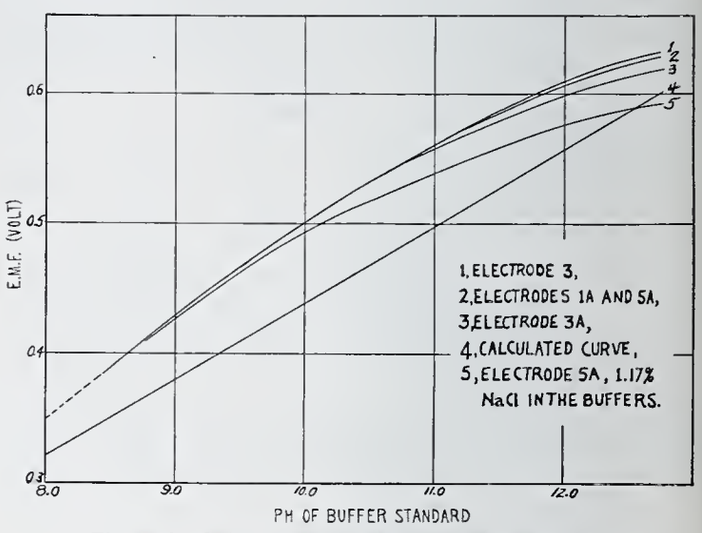


Figure 3—Calibration Curves of Glass Electrodes

Discussion of Results

In the absence of a generally accepted theory it is impossible at the present time to decide whether the pH values determined by the glass electrode are strictly in accordance with those that would be obtained by a hydrogen electrode were it applicable to latex. Hughes (*3*) suggests that the glass membrane acts as a sodium acid silicate buffer which keeps the hydrogen-ion concentration within the glass phase constant. This buffer action begins to become less effective at about pH 9, which is the value at which MacInnes and Dole find deviations begin from the hydrogen electrode. These authors state that when the base present is tetramethylammonium hydroxide there is only a very small deviation even at pH 13. Hughes ascribes the difference in action of the various hydroxides as probably due to greater power of penetrating the glass. Thus potassium hydroxide has less penetrating power than sodium hydroxide owing to the larger potassium ion, and it might be expected that tetramethylammonium hydroxide would have still less penetrating power owing to the large $N(CH_3)_4$ complex.

This leads to the view that the composition of the buffers used in calibrating the electrode should be as far as possible similar to the composition of the solution of which the pH is to be determined. However, in the absence of any data on the relative effects of sodium and ammonium ions on the potential of the glass electrode, the pH values recorded here can be considered provisionally as probably not very far from the true ones.

The two curves in Figure 1 are not strictly comparable as they refer to different latexes, but it is known that the pH values determined by the glass electrode are always higher than corresponding values obtained by means of indicators. The lowest parts of the curves do not differ so much, and in

this region the indicators are more satisfactory, chiefly because their color change for a given increase of hydrogen-ion activity is greater. The increasing divergence between the curves at higher ammonia concentrations might be accounted for partly by loss of ammonia from the serum during filtering. The curves become much flatter at about 0.3 per cent ammonia; this is probably due to acidic substances in the latex.

Literature Cited

(1) Clark, "The Determination of Hydrogen Ions," p. 206, Williams and Wilkins, 1923.
(2) Clark, *Ibid.*, p. 314.
(3) Hughes, *J. Chem. Soc.*, **1928**, 491.
(4) Kerridge, *Biochem. J.*, **19**, 611 (1925).
(5) Lewis, Brighton, and Sebastian, *J. Am. Chem. Soc.*, **39**, 2245 (1917).
(6) MacInnes and Dole, *Ibid.*, **52**, 29 (1930).

Spectrographic Determination of Aluminum in Biological Ashes[1]

Dee Tourtellotte and O. S. Rask

Department of Chemical Hygiene, School of Hygiene and Public Health, Johns Hopkins University, Baltimore, Md.

The principles of the spectrographic method of analysis are discussed and a critical study made of the spectrographic method of qualitative and quantitative analysis with special reference to effects on accuracy and sensitivity of individual radicals and radical mixtures present in the aluminum-containing salts and salt mixtures, and relative merits of the arc and condensed spark methods of excitation.

Modifications are developed of the spectrographic method of quantitative analysis involving both arc and condensed spark methods of excitation.

Tests have been made of the effects of volatility of aluminum compounds on the spectral excitability of the aluminum they contain.

Aluminum has been determined in a number of biological materials using spectrographic technics developed in this investigation.

In an investigation of the role of aluminum compounds in animal physiology and nutrition it became necessary to examine biological ashes for their aluminum contents. This was done by modifications of the spectrographic method as developed by Hartley (*2*), de Gramont (*1*), Meggers (*4*), and others. This method is based on the existence of correlations between low concentrations or quantities of an element in a spectral source (flame, arc, or spark) and the numbers and intensities of certain of its spectral lines especially its *raies ultimes*. It is quite generally recognized that such correlations are materially affected by a number of details in the spectrographic technic so that they can be used for quantitative estimations only when obtained under controlled conditions. However, the literature is lacking in specificity on the extent to which control is necessary. Statements exist to the effect that methods of excitation, time of exposure, and plates used are among the items which effect *raies ultimes* in a spectrogram and must, therefore, be controlled in making quantitative estimations by the spectrographic method. But very little is known concerning the effects on *raies ultimes* of the containing materials and the anions attached to the element determined at the time of excitation, both of which may vary considerably and are more or less beyond control of the operator in estimating aluminum contents of biological ashes by the spectrographic method. The purpose of the experiments here recorded was to ascertain whether these two items, the aluminum-containing material and the anions or negative radicals attached to the aluminum at the time of excitation, possessed effects specific of the containing materials or attached anions, or effects which could be correlated with their properties like alkalinity, acidity, volatility, etc., or whether they possessed no effects whatever on *raies ultimes*, in which case their number and intensities will be due entirely to the concentration of the element which they represent. Publication of these results seems warranted since they may have application in other spectrographic work.

Spectrographic Equipment

Spectrograph—The spectrograph used was Hilger's E-1. This is a quartz prism spectrograph of the Littrow type which disperses the spectrum from 1930 to 8000 Å. over a distance of 30 inches, any 10-inch section of which may be photographed on a 4 by 10 inch (10.16 by 25.4 cm.) plate. Ordinarily the desired portion of the spectrum is not longer than 10 inches, which can be covered in one exposure. The desired portion is obviously that which contains the persistent lines of the element under investigation, which in this case is aluminum. Its most persistent lines are 3944 Å. and 3961.5 Å. with a less persistent pair of lines at 3082 Å. and 3092 Å. On Meggers' authority, obtained by the authors' communication with him, the line 3092 Å. is of no value in this work on account of a nitrogen line of the same wave length.

Spark Hook-Up—The electrical hook-up for producing the high tension spark consisted of a 1.0-kilowatt step-up transformer, ratio 1:200, a variable resistance in series with the primary, a 0.02-microfarad condenser across the secondary, and a self-induction coil in series with the secondary. The variable resistance reduced the primary voltage—i. e., the house current from 118 to 90 volts—which voltage prevented overloading the transformer. The self-induction coil, consisting of 250 turns of No. 20 gage insulated wire on a cardboard tube 5.5 cm. in diameter, served to smooth out the spark discharge and in that way diminished the intensity of the air lines which otherwise would have been present in the spectrum.

Arc Hook-Up—The arc was produced by a 220-volt direct current with a 30.9-ohm resistance in the circuit. This resistance had a carrying capacity of $4^1/_2$ amperes. While a direct current supply of 150 volts is sufficient to maintain an arc between any metallic electrodes, it is highly desirable to use voltages higher than this on account of the fact that arcs between electrodes of material possessing good thermal conductivity tend to extinguish easily.

Electrodes and Electrode Holders—The electrodes used exclusively throughout this work were special aluminum-free copper rods 5 mm. in diameter, supplied as electrodes for this purpose by Hilger. For the spark procedure they were held in a Hilger F 449 adjustable holder in which they were adjusted vertically with respect to one another so that the gap between their points was 7 to 8 mm. The upper electrode was pointed by about a 45-degree taper and the lower

[1] Received October 16, 1930.

electrode was drilled to a depth of 4 mm. with a $^9/_{64}$-inch (0.356-cm.) drill. The resulting hole has a capacity for 20 to 30 mg. of ash material which is considerably more than that used up by the spark in one minute.

In the arc procedure the electrodes were held vertically in a Gaertner arc electrode holder provided with rack and pinion which allowed simultaneous adjustment of the electrodes for striking the arc, followed by simultaneous separation, thereby maintaining stationary the center of the gap. An arc 2 cm. long was necessary to eliminate the continuous spectrum of the incandescent electrode tips. The lower electrode was drilled in the same manner as for the spark, while the upper electrode was left unpointed. Since the positive pole of an arc is the hotter, presumably because of bombardment by electrons from the cathode, better results are obtained by making the lower electrode, which contains the sample, the positive pole.

Plates and Developer—The selection of the photographic plates will obviously vary with the region to be photographed, the source of light, the exposure, and the width of slit. The work in this investigation was confined to the short visible and near ultra-violet region of the spectrum for which Eastman 33 and 36 plates were found satisfactory. The choice between these two plates depended mainly on the width of slit used, the 33 plate being preferred and used for a 0.05-mm. slit, and the 36 plate for a 0.03-mm. slit. In the case of either plate the exposure was 60 seconds for the spark and 15 seconds for the arc.

The plates were developed in a lantern slide formula of elon-hydroquinone selected for its strong contrast effects.

Spectrographic Technic

The spectrograph is first adjusted for the visible portion of the spectrum by the required rotation and focus of the prism. The slit is then opened to the width of about 1 mm., and its middle portion exposed by means of the Hartmann diaphragm. Then the light source, arc or spark, is adjusted laterally and vertically at a distance of about 30 cm. from the slit so that the electrode tips can be seen in the center of the lens field of the spectrograph, after which the slit is closed to a width of about 0.03 mm. and the cylindrical quartz lens interposed between the light source and slit, and adjusted so as to focus the light as sharply as possible on the slit.

In all experiments the Hartmann diaphragm was used. This sliding diaphragm has three apertures which allow the use of three successive portions of the same slit for photography of three comparison spectra without liability of lateral displacement of the spectral lines. The image in passing through the optical system of the spectrograph becomes inverted. Therefore, all spectra were made in 1, 2, 3 order from bottom to top on the diaphragm to give 1, 2, 3 order from top to bottom on the plate. The 1, 2, 3 order on the plate consisted of: (1) control spectrum of cleaned electrodes, (2) spectrum of sample, and (3) addition of element in question as a means of locating the lines, in this case the lines of aluminum.

The electrodes for the spark technic are easily cleaned with 10 to 15 per cent hydrochloric acid. The upper electrode can be used throughout a series of exposures without removing and can be cleaned in position by immersing in the acid and rinsing with a stream of distilled water from a wash bottle. The lower electrode must be removed for cleaning, which must be very thorough for each succeeding spectrogram. The same general procedure was followed for cleaning the arc electrodes, except that a more reactive acid must be used because the higher temperature of the arc tends to fuse the tips of the electrodes so that they may occlude some of the aluminum contained in the previous sample. Cold 25 per cent nitric acid was used for cleaning the arc electrodes, care being taken to confine the more vigorous reaction to the tips. After such cleaning the lower electrode was redrilled, an operation which not only served to reshape it but also to cut away any contaminating material not removed by the cleaning acid.

Experiments

Arc and spark spectrograms were prepared of a series of salts and salt mixtures containing aluminum in concentration from 0 to 1000 p. p. m. The individual salts used for this purpose were: sodium acid sulfate, sodium sulfate, monobasic sodium phosphate, tribasic sodium phosphate, and sodium chloride.

The mixtures used were:

Mixture 1—Tricalcium phosphate, 2 parts; orthopotassium phosphate, 3 parts; sodium sulfate, 1 part; magnesium sulfate, 1 part.

Mixture 2—Orthopotassium phosphate, 1 part; potassium sulfate, 1 part; tribasic sodium phosphate, 1 part.

Mixture 3—Tricalcium phosphate, 1 part; magnesium sulfate ($MgSO_4.7H_2O$), 1 part.

In preparing the several series of aluminum concentrations in the above salts and salt mixtures, the calculated volume of an aluminum ammonium sulfate, $Al_2(SO_4)_3(NH_4)_2SO_4.24H_2O$, solution containing 0.01 to 0.1 per cent of the element aluminum was in each case added and mixed into the required weight of the salt or salt mixture contained in a 50-cc. Pyrex beaker. For example, in preparing a concentration of 5 p. p. m. of aluminum in any of the above salts, 1.0 cc. of a 0.01 per cent solution of aluminum in the form of the aluminum ammonium sulfate was added and mixed into 2 grams of the salt contained in a 50-cc. Pyrex beaker. The material was then dried at 110° C. Just previous to spectral excitation the material was pulverized and mixed again by means of a cleaned copper electrode.

The single salts represent the anions as variables and in combination with a common cation—viz., sodium. Mixture 1 was composed to represent a biological ash. Its composition approximates that of biological ashes. Mixture 2 is intended to show the effects of cations of the first group of the periodic system, the members of which have low ionization potentials. Mixture 3 represents cations of the second group of the periodic system. These have somewhat higher ionization potentials than those of the first group.

Spectrograms were prepared of these mixtures by the technic already described. The results are given in Table I, in which the conventions used denote the following line intensities:

Completely invisible by lens	−
Questionably visible by lens or of same intensity as electrode control	±?
Visible by the aid of the lens	±
Visible to naked eye as a light line (without the aid of the lens)	+
Visible to naked eye as a heavy line (without the aid of the lens)	++
Sufficiently heavy to cause a fogged line	+++

A study of Table I shows that in practical use correlations between aluminum concentrations and aluminum lines are unaffected by the radicals which constitute the aluminum-containing materials.

As has already been stated for the above aluminum-containing salt mixtures, the aluminum, in the form of very dilute solutions of aluminum ammonium sulfate containing 0.01 and 0.1 per cent of the element aluminum, was added and mixed into a weighed quantity of the salt mixture which was then evaporated to dryness at 110° C. previous to arcking or

Table I—Effect of Anions on Correlation between Spectral Effects and Aluminum Concentration in Sodium Salts

Salt	Aluminum Concentration		Arc			Spark		
	Ash basis	Fresh[a] tissue basis	3082 Å.	3944 Å.	3961.5 Å.	3082 Å.	3944 Å.	3961.5 Å.
	P. p. m.							
$NaHSO_4$	Control		−	−	−	−	−	−
	25	0.25	±?	+	+	−	+	+
	50	0.5	±	++	++	−	+	+
	100	1.0	±	+	+	−	+	+
	200	2.0	+	++	++	±	+	+
	500	5.0	+	++	++	+	++	++
Na_2SO_4	Control		−	−	−	−	−	−
	25	0.25	−	±	+	−	±	+
	50	0.5	−	+	+	−	+	+
	100	1.0	±	+	+	−	±	+
	200	2.0	−	−	−	−	±	+
	500	5.0	+	++	++	±	+	+
NaH_2PO_4	Control		±?	+	+	−	−	±
	25	0.25	−	±	+	−	±	+
	50	0.5	±?	+	+	−	±	±
	100	1.0	±?	+	+	−	+	+
	200	2.0	±?	±	+	−	+	+
	500	5.0	±?	+	+	+	+	++
Na_3PO_4	Control		−	−	−	−	−	−
	25	0.25	−	±	+	−	−	−
	50	0.5	±	+	+	−	±	+
	100	1.0	±	+	+	−	±	+
	200	2.0	±	+	+	−	±	+
	500	5.0	±	++	++	−	−	±
NaCl	Control		−	−	−	−	−	−
	25	0.25	−	−	±	−	±	+
	50	0.5	±	+	+	±	+	+
	100	1.0	±	+	+	+	+	+
	200	2.0	±	++	++	+	++	++
	500	5.0	±	++	++	+	++	++
Mixture 1	Control		−	−	±	−	−	±?
	5	0.05	−	−	±	−	−	±
	10	0.1	−	−	±	−	±	±
	20	0.2	−	−	±	−	±	+
	50	0.5	−	±	+	−	±	+
	100	1.0	−	+	+	−	+	+
	200	2.0	−	+	+	±?	+	+
	500	5.0	±?	+	++	±?	+	+
	1000	10.0	±	+	++	±	+	++
Mixture 2	Control		−	−	−	−	−	±?
	5	0.05	−	−	±	−	−	±
	10	0.1	−	−	±	−	−	+
	20	0.2	−	±?	+	−	−	+
	50	0.5	−	±	+	−	−	+
	100	1.0	−	+	+	−	−	+
	200	2.0	−	+	+	±?	+	+
	500	5.0	−	+	+	±	+	+
	1000	10.0	±	+	+	±	+	+
Mixture 3	Control		−	−	±?	−	−	±?
	5	0.05	−	−	±	−	−	±
	10	0.1	−	±?	+	−	−	±
	20	0.2	−	±?	+	−	−	+
	50	0.5	−	±	+	−	−	+
	100	1.0	±	+	+	−	−	+
	200	2.0	±	+	+	±?	±	+
	500	5.0	+	+	+	±	+	+
	1000	10.0	++	++	++	±	+	+

[a] Fresh tissue containing about 1 per cent ash.

sparking. Accordingly, the aluminum itself must have existed in the form of a salt of the predominating anion in the mixtures. Since these anions showed no effect on the relationship or correlation between aluminum concentration in the spectral source and spectral results—i. e., aluminum lines—it may also be concluded that the anion attached to aluminum itself has no effect on this relationship. However, in order to confirm this conclusion, arc and spark spectra were prepared of 1.0, 0.1, 0.01, and 0.001 mg. of aluminum introduced into the spectral sources (the arc and the spark) as chlorides in one series, as oxides in another series, and as phosphates in a third series. Correlations in the resulting spectrograms were then compared. The experimental procedure in this comparative study was as follows:

Aluminum Chloride Spectrograms—A series of aluminum chloride solutions were prepared containing, respectively, 1.0, 0.1, 0.01, and 0.001 mg. of the element aluminum per 0.05 cc. (one drop) of solution. Arc and spark spectrograms were prepared of the residues of one drop of each of these solutions. The one-drop residues were obtained in the cup of the lower electrode by introducing one drop of the solution into the cup and then evaporating its water content by holding the electrode vertically in one hand and playing a small flame of a micro burner along the side of the electrode by means of the other hand until evaporation became visible. The flaming was always stopped before the upper portion of the electrode became too hot to be held in the bare hand. In that manner an evaporating temperature higher than 70° or 75° C. was avoided. At such temperatures the drop evaporated to apparent dryness in less than 2 minutes and presumably without any decomposition of aluminum chloride. The spectrograms of the one-drop residues prepared in this manner are recorded in Table II in which they are identified as aluminum chloride spectrograms.

Aluminum Oxide Spectrograms—The above aluminum chloride solutions were used as sources of aluminum in preparing arc and spark spectrograms of the corresponding or same quantities of aluminum in form of the oxide. The experimental technic was the same as that followed in preparing the above aluminum chloride spectrograms except that one drop of concentrated ammonia was added to each of the several one-drop residues of the aluminum chloride solutions just before these residues reached complete dryness in the holes of the lower electrodes. The evaporation was then continued and completed with the necessary precautions to prevent spattering, after which the upper end of the electrode was heated nearly to a dull redness in order to render the residue chloride-free, in which condition it was then excited. The spectrograms of these residues are recorded and identified in Table II as aluminum oxide spectrograms.

Aluminum Phosphate Spectrograms—In preparing arc and spark spectrograms of the same quantities of aluminum in the form of the phosphate, the source of aluminum was an aluminum phosphate solution in 7 to 8 per cent phosphoric acid which contained 1.0 mg. of aluminum per 0.05 cc. (one drop) of solution. From this solution dilutions were made containing, respectively, 0.1, 0.01, and 0.001 mg. of aluminum per 0.05 cc. of solution. Water was used in making these dilutions so that the original 7 to 8 per cent phosphoric acid was diluted correspondingly. One-drop residues of these solutions were prepared in the cup of the lower electrode in the same manner as that followed in the case of the chloride solutions except that the residues from the original undiluted solution, that containing 1.0 mg. of aluminum per 0.05 cc. of undiluted 7 to 8 per cent phosphoric acid, were heated nearly but cautiously to dull redness previous to excitation. The spectrograms of these residues are recorded and identified in Table II as the aluminum phosphate spectrograms.

Table II—Effect of Form of Combination of Aluminum on Correlation between Spectral Effects and Aluminum Concentration

Sample	3082 Å.			3944 Å.			3961.5 Å.		
Arc	$AlCl_3$	Al_2O_3	$AlPO_4$	$AlCl_3$	Al_2O_3	$AlPO_4$	$AlCl_3$	Al_2O_3	$AlPO_4$
Mg.									
0.001	±?	±?	±?	±	+	+	+	±	+
0.01	±?	±	+	+	+	+	+	+	+
0.1	+	+	+	++	++	++	++	++	++
1.0	++	++	++	++	++	++	++	++	++
Spark									
0.001	+	+	+	+	+	+	+	+	+
0.01	+	+	+	+	+	+	+	+	+
0.1	+	+	+	++	++	++	++	++	++
1.0	++	++	++	++	++	++	++	++	++

An inspection of Table II shows that chlorides, oxides, and phosphates of aluminum produce equivalent correlations between aluminum lines and quantities of the element aluminum in the spectral source excited by either the arc or the spark. The results in these tables, therefore, warrant the conclusion that the negative radical attached to aluminum

in the spectral source at the time of excitation does not affect the correlations between the quantities and presumably also the concentrations of aluminum in the spectral source, and the aluminum lines in the resulting spectrograms. Accordingly, the numbers and intensities of the aluminum *raies ultimes* are due entirely to the quantity or concentration of aluminum in the spectral source and independent of the radicals attached to the aluminum.

The view has been expressed that the excitability of the aluminum spectrum may vary with the volatility of the aluminum compound in the spectral source—that is, with the volatility of chemical form or combination in which aluminum is excited, whether excitation be by the arc or by the condensed spark. Accordingly, the aluminum spectrum will be very readily and completely excited when the aluminum is present in the spectral source in the form of a volatile compound like aluminum chloride, and will escape excitation more or less entirely when the aluminum is present in the spectral source in form of a relatively non-volatile compound like aluminum phosphate. However, the results in Table II also show that volatility of the form in which aluminum occurs in the spectral source does not affect or determine the sensitiveness of the spectrographic method for detecting the presence or absence of small amounts of aluminum either by the arc or spark methods of excitation. In connection with these tests it is a well known fact that hydrated aluminum chloride when heated to dryness yields the non-volatile oxide of aluminum.

The sensitivity of the method is demonstrated by the extremely small quantities of aluminum detected by either the arc or the spark as shown by the data in Table II, and by the extremely low concentrations of aluminum which are detected in the salt mixtures. In these materials 5 p. p. m. of aluminum were sufficient to produce the aluminum line 3961.5 Å. This concentration is equal to 0.05 p. p. m. of aluminum of fresh biological tissue of which the ash is 1 per cent. An ash content of 1 per cent has been assumed in computing p. p. m. of aluminum on the basis of fresh tissues. The data contained in the above tables show both from the standpoint of sensitivity and quantitative correlations that the arc and spark agree very well over the range investigated.

Determination of Aluminum in Biological Material

In ascertaining the presence or absence of an element so common in its occurrence as aluminum, more than ordinary cleanliness was exercised. Such cleanliness was practiced throughout the entire procedure, including the isolation or the dissection of the biological sample. Materials such as potatoes were thoroughly washed in distilled water and peeled twice with a nickel-plated knife which had been washed in distilled water. The potato was washed between peelings and again before placing in the cleaned silica dish for ashing.

Equally extreme precautions were exercised in the collection of rat organs. The thorax and abdomen were skinned from a mid-line incision, using care to keep hair and foreign material from the exposed abdomen and thorax. The abdomen and thorax were then opened with nickel-plated instruments previously cleaned in distilled water. The organs were removed with clean instruments and washed in a stream of distilled water before being placed in the clean silica dishes.

Eggs were washed in distilled water and dried with filter paper before breaking into clean Pyrex beakers. The samples represent homogeneous mixtures of white and yolk obtained by whipping the egg in the beaker with a glass rod.

Isolation or dissection of the material for analysis was followed immediately by its ashing, which served the purpose of concentrating the sample by removal of the organic matter. All samples were ashed by a technic which was essentially the same as that described by McCollum, Rask, and Becker (*3*). The material was ashed in silica dishes supported on silica or nichrome triangles over Bunsen flames. In all cases the material was ashed in the shortest possible time in a room with little disturbance to avoid as completely as possible contamination by dust.

It was impossible to obtain carbon-free ashes from animal tissues. An attempt was made to burn the carbon completely by passing a stream of oxygen through a specially bent silica tube into the ash mixture at different stages of the ashing process, the ashing being carried out in silica crucibles or beakers of about 50 cc. capacity. The oxygen was previously purified by passing through a wash train of concentrated sulfuric acid. It was found that the combustion could not be controlled in such a procedure and this experiment resulted in a fusion of the ash to the silica dish. Even though the carbon was completely burned, the procedure had to be abandoned on account of the fusion.

The ash was therefore subjected to the spectrographic technic as already described. Both arc and spark spectrograms were prepared of most ashes, so that results obtained by each method of excitation could be compared with the results obtained by the other method of excitation.

Table III—Spectral Effects with Aluminum Concentrations in Various Biological Materials

Material	Arc			Spark		
	3944 Å.	3961.5 Å.	Aluminum concentration in fresh tissue	3944 Å.	3961.5 Å.	Aluminum concentration in fresh tissue
			P. p. m.			*P. p. m.*
Rat[a]	+	+	0.5 to 1.0	−	±	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±?	0.05
	+	+	0.5 to 1.0	−	±	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	−	−	0.05	−	−	0
Egg	±	+	0.5	−	±?	0.05
	−	±	0.2	−	±?	0.05
	−	+	0.5	−	±?	0.05
	−	+	0.5	−	±?	0.05
	−	+	0.5	−	±?	0.05
	±	+	0.5	−	±?	0.05
	−	−	0.05	−	−	0
Thyroid	+	+	2.0			
	+	+	2.0			
	+	+	2.0			
Potato	−	−	0.05	−	±	0.05
	−	±?	0.05	−	±	0.05
	−	−	0.05	−	±	0.05
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	−	0
	−	±?	0.05	−	±	0.05
Carrot	−	±?	0.05	−	±	0.05
Nut	−	±	0.05	−	−	0

[a] Each rat is represented by its liver, kidneys, spleen, and testes or ovaries.

Table III contains the results of the spectrographic determinations of aluminum in biological materials. The arc and spark lines are recorded separately and in terms of the conventions defined above. The lines obtained by each method of excitation have been translated into the parts of aluminum per million of fresh tissue which they represent according to the respective arc and spark standard spectrograms given in the last three parts of Table I.

Rat viscera as listed in Table III consist of the combined liver, kidneys, spleen, and testes or ovaries of one adult and

apparently healthy rat raised on stock diet. The arc method of excitation shows 0.5 to 1.0 p. p. m. of aluminum in the viscera of six rats; not more than 0.5 p. p. m. of aluminum in the viscera of six other rats and less than 0.05 p. p. m. of aluminum in the viscera of one rat. The spark method of excitation resulted in only a faint image of one single line, 3961.5 Å., in each of these same thirteen sets of rat viscera. This weak spectral effect represents, according to the spark standards, only 0.05 p. p. m. of aluminum. Such a difference between the results of the arc and spark methods of excitation is inconsistent with the results of these two methods of excitation obtained on the aluminum standards listed in the second section of Table I. As shown by this data, the arc and spark methods of excitation produce lines equivalent to one another in each of the aluminum standards containing the same concentration of aluminum over the range from 0 to 1000 p. p. m. of aluminum and the same variations in aluminum lines with variations in aluminum concentrations over this range, indicating that no differences exist between the arc and spark methods of excitation either in sensitivity or in correlations with aluminum concentrations. However, the lower concentrations of aluminum indicated in rat viscera by the spark method of excitation suggest that this method of excitation is for some reason not applicable to the ashes of rat viscera, or rather to the ashes of rat viscera in the condition in which they were excited.

The egg samples represent individual whole eggs, exclusive of shell, obtained from different markets on different days. The arc method of excitation shows a concentration of not more than 0.5 p. p. m. of aluminum in five of the egg ashes listed in Table III, a concentration of approximately 0.2 p. p. m. of aluminum in one of the two remaining egg ashes, and less than 0.05 of aluminum in the other. The spark method shows a concentration of aluminum of less than 0.05 p. p. m. in all seven of these same egg ashes. Accordingly, the spark method of excitation also shows lower concentrations of aluminum in egg ashes than does the arc method, although the differences between the two methods of excitation are not quite so large in the case of egg ashes as in the case of the ashes of rat viscera.

The ten potatoes listed in Table III are samples of medium-sized potatoes purchased on different days from five or six different markets. The one carrot listed in the table was a sample of a medium-sized apparently healthy carrot prepared as previously described. The walnut listed in the table represented the meats of four apparently healthy English walnuts prepared with the same precautions. All of these twelve samples show practically the same concentrations of aluminum by both the arc and spark methods of excitation. These concentrations are less than 0.05 p. p. m. in nine of the ten potatoes, and approximately 0.05 p. p. m. in one potato, the carrot, and the walnut.

The main purpose of the data in Table III was to ascertain the width and the abundance of the distribution of aluminum in biological matter. For such purposes these data may seem limited, due to the limited number of materials examined. However, the variety and the character of the materials are such as to warrant the conclusion that the concentrations of aluminum in biological matter must invariably be very low.

Tha nature of the spectrographic method of analysis is such that error seems possible only in one direction, that of producing aluminum lines when little or no aluminum is present in the sample, in which case aluminum lines will be due to aluminum from outside sources such as atmospheric dust introduced during the ashing process. Such errors are, to say the least, highly probable, due to the wide spread occurrence of aluminum and to the small amount ncesssary to produce aluminum *raies ultimes*. On the other hand, it is inconceivable that aluminum actually present will ever fail to produce aluminum lines when excitation is properly done. If it is assumed that errors in the spectrographic detection or estimation of aluminum will invariably be one-sided in the above manner, then the lowest concentrations reported in Table III will be the more nearly correct ones. The writers are inclined to this view as a result of 2 years' experience with spectrographic methods of quantitative analysis.

No complete or otherwise satisfactory explanation is available for the above observed inconsistencies in the relation between the performances of the arc and spark methods of excitation. The lower concentrations of aluminum indicated in rat viscera by the spark may have been due to unburned carbon which was always present in their ashes, since potato ashes, on which the two methods agree more nearly, were practically free from carbon. Carbon was also, of course, completely absent from the aluminum standards in which the two methods gave identical results. Carbon particles might tend to occlude any aluminum present which would be liberated by burning of the carbon at the high temperature of the arc. Apparently, therefore, the spark method of excitation is not applicable to ashes containing unburned carbon, whereas the arc method is. Further experimental work is required to explain these inconsistencies.

Aluminum in Chemically Pure Reagents

In connection with this study arc spectrograms were prepared of a number of C. P. labeled inorganic salts. The salts were selected from unopened bottles which gave no declaration of aluminum on the label. Salts whose labels declared the presence of aluminum were specifically excluded from the test. The results are recorded in Table IV and show that in the case of such highly purified products as chemically pure reagents detectable amounts of aluminum may occur in a large percentage of the samples, in this case about 50 per cent.

Table IV—Aluminum *raies ultimes* Produced by C. P. Labeled Reagents

Sample	Arc	
	3944 Å.	3961.5 Å.
Lithium sulfate	−	±
Sodium sulfate	−	±
Sodium thiosulfate	−	−
Sodium iodide	−	±
Potassium nitrate	−	−
Potassium sulfate	−	−
Potassium chloride	±	+
Cupric chloride	+	+
Magnesium chloride	−	−
Calcium phosphate	−	±?
Barium carbonate	−	±?
Manganous sulfate	−	±?
Manganous chloride	−	+
Ferric phosphate	−	+
Ferrous ammonium sulfate	−	−
Ferrous chloride	−	±?
Nickel chloride	+	+

Conclusions

The spectrographic method of analysis is capable of detecting the presence of 5 p. p. m. of aluminum in all of the several kinds of salts and salt mixtures on which the sensitivity of the spectrographic method was tested.

The spectrographic method of analysis will determine quantitatively, with an error of ±25 per cent, concentrations of aluminum ranging from 0.5 to 1000 p. p. m. in inorganic materials, including biological ashes.

The arc and the condensed spark methods of excitation appear to be equally satisfactory when applied to the several salts and salt mixtures used in this investigation as aluminum-containing materials. These two methods of excitation also appear to be equivalent to one another for determining aluminum in certain biological ashes, but in other biological

ashes, especially those containing unburnt carbon, the arc method seems more sensitive and the spark less so. The presence of carbon seems to reduce the sensitiveness of the spark method of excitation but not the sensitivity of the arc method, so that the spark is not so satisfactory in its applicability to biological ashes containing unburnt carbon, as the arc.

There is no noticeable relationship between the volatility of the form in which aluminum occurs in the spectral source and the sensitivity of its spectrographic detection either by the arc or the condensed spark methods of excitation.

Chemical composition of aluminum-containing salts and salt mixtures does not affect correlations between aluminum concentrations and spectral effects. That is, these correlations are independent of the composition of the aluminum-containing salts or salt mixtures.

About one-half of the C. P. labeled reagents examined contained traces of aluminum detectable by the spectrographic method.

Literature Cited

(1) Gramont, de, *Compt. rend.*, **144**, 1101 (1907).
(2) Hartley, *Phil. Trans.*, **175**, 325 (1884).
(3) McCollum, Rask, and Becker, *J. Biol. Chem.*, **77**, 753 (1928).
(4) Meggers, Kiess, and Stimson, Bur. Standards, *Sci. Paper* **444** (1922).

A Mill for Small Samples[1]

W. H. Cook, E. P. Griffing, and C. L. Alsberg

FOOD RESEARCH INSTITUTE AND DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, CALIF.

THE elaborate system of microanalysis developed by organic chemists for the analysis of homogeneous material has been largely inapplicable to biological solid materials, owing to the difficulty of grinding and sampling a micro-quantity of such material without loss of substance or moisture. The authors were confronted with the problem of analyzing individual wheat leaves, necessitating the use of semi-microchemical methods, and the preparation of this material for analysis required a grinder capable of reducing small quantities of substance without loss. The grinding of such material is extremely difficult because of its fibrous nature.

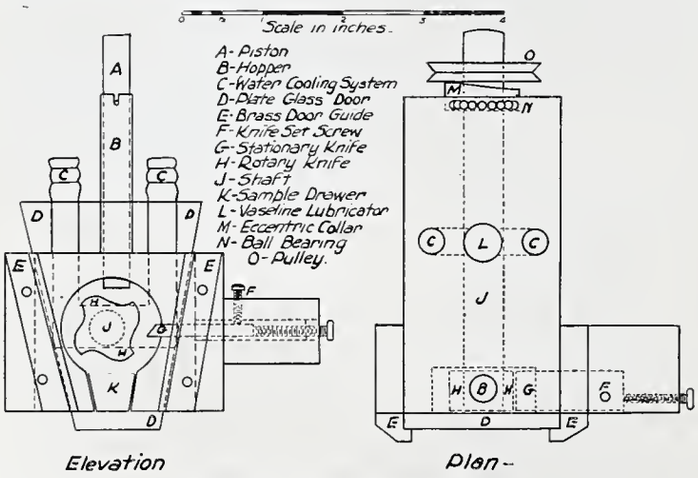


Figure 1—Micro-Grinding Mill

For this purpose a mill was designed on the general cutting principle of the Wiley laboratory mill (*2*), but many modifications in construction were necessary because of the greatly reduced size. A rapid shearing effect is obtained by the action of a hard tooled steel knife with four blades keyed to a shaft, cutting against one blade of tooled steel placed in the wall of the grinding chamber. The rotating knife also serves to keep the material in motion, and when it has been ground sufficiently, aids in its discharge through a screen in the bottom of the chamber.

Dimensions

The main body of the mill, as diagramed in Figure 1 and pictured in Figure 2, consists of a cast-iron block 2 inches square and 4 inches long, $3^1/_2$ inches of which are occupied by the bearing for the half-inch shaft. The front half inch forms the grinding chamber which is $1^1/_4$ inches in diameter, and the rotating knife, *H*, keyed to the shaft, *J*, occupies about three-quarters of its capacity. The length of the rotating blades from the center of the shaft is $^1/_2$ inch. The stationary blade, *G*, is attached to the wall of the chamber in such a manner as to allow different clearances between the blades, or to take up wear from sharpening. A brass tube, *B*, $^7/_{16}$ inch in diameter leads into the top of the grinding chamber for introducing the material, and is closed during grinding by means of a solid brass piston, *A*, which is pinned to prevent its dropping on the knife during grinding. The bottom of the chamber is formed by a copper drawer, *K*, which acts as a receptacle for the ground material. The top of the drawer consists of a piece of mesh of the desired size, $^8/_{16}$ by $^{11}/_{16}$ inch in dimension. The sides of the drawer slant to a narrower base to prevent the drawer from dropping out, and a snug fit to the main frame keeps the ground material from sifting out during grinding. The front face of this drawer is open to permit removal of the sample and is closed during operation by the plate glass front of the grinding chamber. This glass door fits tightly by being ground to fit brass guides fastened to the main frame, and allows easy access to the grinding chamber for cleaning, as well as permitting one to see the grinding operation. Around the shaft at the opposite end from the grinding chamber is a ball bearing to take out sideplay and prevent wearing due to the high speed of the mill. The rest of the shaft between the

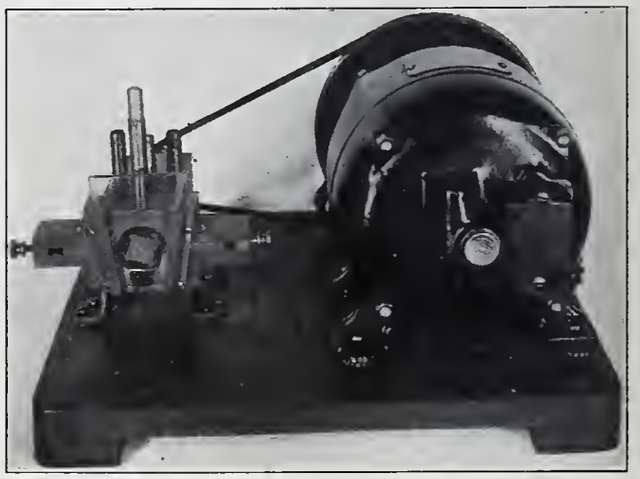


Figure 2—Mill for Small Samples

[1] Received November 7, 1930.

ball bearing and grinding chamber is surrounded by babbitt metal. It is lubricated by vaseline through a hole in the center of the bearing and is driven by a 1-inch pulley attached to the end opposite the grinding chamber.

Operation

One of the difficulties encountered in early trials was that of keeping the material in motion. The small size of the rotating knife made it necessary to drive the mill at the rate of 5600 r. p. m. to give sufficient surface speed to keep the material agitated. A plug of metal (not shown in Figure 1) to fill in the angle between the wall of the grinding chamber and the stationary blade helped to prevent the material from gathering at that point. The use of more than the one stationary blade in the wall of the chamber in order to increase the cutting speed of the mill is impossible due to the tendency of the material being ground to gather on the top of the blade. A slightly eccentric collar was placed on the shaft at the pulley end to furnish enough vibration to ensure that the finely ground material would pass through the sieve.

Since a temperature increase during grinding might be detrimental to the material by causing moisture loss, etc., the mill was provided with a water-cooling system surrounding the shaft. So far it has been unnecessary to use it, as the large bulk of iron in the main body of the mill tends to take up and conduct away the small amount of heat developed.

A second experimental mill made with a smaller body did need a water-cooling system to prevent overheating. A nickel-plated brass face was used for that portion containing the grinding chamber.

This grinding mill has been found very satisfactory for grinding small samples of material difficult to grind. In grinding wheat kernels it is necessary to break them up in a mortar to prevent them from tearing the copper mesh by hitting it too suddenly. It is better to cut leaves, also, into rather small pieces convenient for loading. The capacity of the mill is about five to eight kernels of wheat or several wheat leaves at one charge, and the operation can be performed practically without loss of material, with proper precautions, so that a representative sample may be obtained for microanalysis. It is rapid in operation. At an operating speed of 5600 r. p. m. and a clearance of $^1/_{2000}$ inch between the rotating and stationary blades, a single charge of material is reduced to pass an 80-mesh sieve in from 3 to 4 minutes. The simplicity and accessibility of the grinding chamber permits thorough and rapid cleaning between samples. The homogeneity of ground wheat leaves or kernels has been demonstrated by more than 200 analyses for total nitrogen content, successive 20-mg. samples having been found to check within a few hundredths of 1 per cent of nitrogen. Analyses were made according to the ter Meulen and Heslinga hydrogen method (*1*).

The Arthur H. Thomas Company of Philadelphia has designed and is about to place on the market a micro-grinding mill involving the main principles of construction of the mill described in this article.

Literature Cited

(1) Meulen, ter, and Heslinga, "Neue Methoden der organisch-chemischen Analyse," Akademische Verlagsgesellschaft, 1927
(2) Wiley, Ind. Eng. Chem., **17**, 304 (1925).

Determination of Aluminum in Ferrochromium and Chromium Metal[1]

Thos. R. Cunningham

Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y.

IN THE following method iron is separated by means of cupferron while chromium is oxidized by evaporating the solution with perchloric acid, and aluminum is separated by precipitation with ammonia.

Two and one-half grams of the sample are transferred to a 250-cc. covered beaker and treated with 15 cc. of hydrochloric acid (sp. gr. 1.19). If the aluminum content is less than 0.1 per cent it is necessary to work on a 10-gram sample. This is accomplished by dissolving four 2.5-gram portions of the sample and subsequently combining the four aluminum hydroxide precipitates, obtained as described below, by filtering on a single 9-cm. paper and washing with a 2 per cent ammonium chloride solution. The solution is warmed to about 60° C. until all action has ceased, when 3 cc. of Perhydrol (30 per cent hydrogen peroxide) are added and the liquid boiled down to a sirup. Thirty cubic centimeters of hydrochloric acid (1 to 1) are introduced, the solution heated until all salts have dissolved, diluted with water to 50 cc. and filtered on a 9-cm. paper containing some ashless paper pulp into a 400-cc. beaker, and reserved. The paper and residue are washed 18 to 20 times with hot water and ignited in a 30-cc. platinum crucible. Five drops of sulfuric acid (1 to 1) and 2 cc. of hydrofluoric acid (48 per cent) are introduced and the silica is volatilized by evaporating the solution to the complete expulsion of the acids.

[1] Received October 16, 1930.

The residue is fused with 2 grams of sodium carbonate and the melt dissolved in 25 cc. of hot sulfuric acid (1 to 4). If four 2.5-gram portions are taken for analysis the residues may be combined and only one fusion made, increasing, of course, the weight of sodium carbonate used to 8 grams. The solution is boiled to expel carbon dioxide, approximately 2 grams of ammonium chloride and a very faint excess of dilute filtered ammonium hydroxide (1 to 3) are then introduced, and the solution is boiled for no longer than 1 or 2 minutes. The precipitate is filtered on a 9-cm. paper containing some ashless paper pulp and washed thoroughly with hot 2 per cent ammonium chloride solution. The paper holding the precipitate is transferred to the 400-cc. beaker containing the main solution and macerated to a pulp by means of a glass rod. The liquid is then heated just short of boiling for about 5 minutes to insure the complete solution of the precipitate.

The solution (which should have a volume of about 100 cc. and an acidity of approximately 15 per cent) is cooled to approximately 15° C. and the iron precipitated by the addition of a slight excess of a freshly prepared, cold 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5(NO)ONH_4$), while all aluminum and chromium will remain in solution. A brownish red, partly amorphous, partly crystalline, precipitate separates out. As soon as a drop of the reagent causes the formation of a transient snow-white crystalline precipitate, all of the iron is down. The

solution is filtered on an 11-cm. paper containing some ashless paper pulp, the paper and precipitate washed well with cold 5 per cent hydrochloric acid, and discarded.

The filtrate and washings are collected in a 600-cc. beaker and boiled down to a volume of about 50 cc. Fifty cubic centimeters of nitric acid (sp. gr. 1.42) are introduced and the boiling continued until the volume has been reduced to approximately 10 cc. Twenty cubic centimeters of nitric acid (sp. gr. 1.42) and 30 cc. of perchloric acid (60 per cent) are added, the solution evaporated to strong fumes of perchloric acid, and heated for an additional 30 minutes to insure the complete oxidation of the chromium to chromic acid. One hundred cubic centimeters of water are introduced, the solution is warmed, filtered on a 9-cm. paper, and the silica washed with warm water. The filtrate and washings, which should not exceed 175 cc., are collected in a 400-cc. beaker.

The solution is nearly neutralized with filtered ammonium hydroxide (1 to 3) and heated to boiling. Approximately 5 grams of ammonium chloride and some ashless paper pulp are added and the solution treated with dilute ammonium hydroxide (1 to 3) drop by drop until the color just changes to a distinct yellow. The solution is boiled for no longer than 1 or 2 minutes and immediately filtered on a 9-cm. paper. The paper and precipitate are washed thoroughly with hot 2 per cent ammonium chloride solution, transferred to a 150-cc. beaker and treated with 15 cc. of hydrochloric acid (1 to 2). The solution is heated to boiling for several minutes, diluted with warm water to 100 cc., and treated with a brisk stream of hydrogen sulfide for 15 minutes to precipitate platinum. Any precipitate that forms is filtered on a 9-cm. paper, washed 10 to 12 times with hydrogen sulfide water containing 1 per cent hydrochloric acid, and discarded.

The filtrate contained in a 400-cc. beaker is boiled to expel hydrogen sulfide, 5 cc. of perchloric acid (60 per cent) are added, and the solution is evaporated to strong fumes of perchloric acid and heated for an additional 15 minutes. One hundred cubic centimeters of warm water are added and the solution is nearly neutralized with filtered ammonium hydroxide (1 to 3) and heated to boiling. Approximately 2 grams of ammonium chloride, some ashless paper pulp, and several drops of an 0.2 per cent alcoholic solution of methyl red are introduced and the solution treated with dilute filtered ammonium hydroxide (1 to 3) drop by drop until the color just changes to a distinct yellow. The solution is boiled for no longer than 1 or 2 minutes and immediately filtered on a 9-cm. paper. The paper and precipitate are washed thoroughly with hot 2 per cent ammonium chloride solution.

The precipitate is ignited in a weighed platinum crucible first at a low temperature and finally over a blast lamp for 5 minutes or in an electric furnace at 1150° C. for 15 minutes. The crucible covered with a closely fitting lid is allowed to stand in a desiccator until cool and then rapidly weighed. A second heating of equal duration is advisable, especially as it permits more rapid weighing and consequently more accurate results. Ignited alumina is very hygroscopic, and absorbs within the first 10 minutes' exposure to the air a large proportion of the total water which it will take up in 24 hours. A well-fitting crucible cover is quite efficient in preventing the adsorption of moisture by the alumina while the crucible is in the desiccator or on the balance pan.

Elimination of Phosphorus

The precipitate obtained as described will contain part or all of the phosphorus in the alloy (depending upon the aluminum content) but rarely contains chromium; should it be colored, indicating the presence of chromium sesquioxide, it is fused with 1 to 2 grams of sodium carbonate. The melt is dissolved in the least necessary amount of hot water and the chromium determined colorimetrically. A small amount of sodium peroxide is added and the liquid is boiled for a few minutes and cooled. The chromate solution is transferred to a Camp comparison tube. The volume should now be about 15 cc. To the other comparison tube there is added from a 10-cc. buret an amount of standard potassium chromate solution (1 cc. = 0.00050 gram Cr.) which contains slightly less chromium than the sample, and sufficient water to make their volumes exactly equal. After having mixed each, the intensity of the two solutions is compared. The color of the sample should be slightly more intense than that of the standard. An additional small amount of the standard chromate solution is added to the tube containing the standard, and an equal amount of water to the tube holding the sample. After having mixed the contents of the tubes the intensities of the colors are again compared. These operations are repeated until an exact match is obtained. The number of cubic centimeters of the chromate solution used, multiplied by 0.00050, multiplied by 1.4615, gives the weight of chromium sesquioxide to be deducted.

After having determined the chromium colorimetrically, the solution from the sodium carbonate fusion is transferred to a 300-cc. Erlenmeyer flask and made acid with an excess of 2 cc. of nitric acid (sp. gr. 1.42). The solution is heated to boiling to expel carbon dioxide and the chromium reduced to the trivalent state by the addition of a sufficient amount of sulfurous acid, and by boiling. The liquid is cooled to 40° C., approximately 5 grams of ammonium nitrate, 0.05 gram of ferrous sulfate (free from phosphorus), and 40 cc. of molybdate solution added, and the phosphorus precipitated as ammonium phosphomolybdate by 5 minutes of vigorous shaking. The precipitate is allowed to settle and the phosphorus is determined by either the alkalimetric or the molybdenum reduction (Emmerton) method. The weight of phosphorus found, multiplied by 2.2887, is the weight of phosphorus pentoxide to be deducted from the weight of the alumina precipitate.

The weight of the alumina precipitate, less the weights of chromic oxide and phosphorus pentoxide found, is multiplied by 52.94 and divided by the weight of sample taken to give the percentage of aluminum in the alloy.

A blank should be run on all the reagents used and any aluminum found deducted from the result obtained as above described.

Experimental Proof of Accuracy of Method

In order to test the accuracy of the method a number of experiments were carried out. The procedure consisted in salting several samples of the Bureau of Standards standard sample 64 of high carbon ferrochromium[2] with varying amounts of pure aluminum chloride. The accurately measured aliquot portions of the standard solution of pure aluminum chloride were added to the weighed samples of ferrochromium, which were then dissolved and otherwise treated as given in the description of the method. The results obtained are shown in the table.

Experiments to Test Accuracy of Method

Experiment	Ferrochromium Taken *Grams*	Aluminum Added *Gram*	Aluminum Found *Gram*	Aluminum Recovered[a] *Gram*	Error *Gram*
1	5	Nil	0.00105		
2	5	Nil	0.00100		
3	10	Nil	0.00220		
			Av. 0.021%		
4	5	0.00228	0.00339	0.00234	+0.00006
5	5	0.0039	0.00498	0.00393	+0.00003

[a] After correcting for 0.021 per cent Al in alloy.

[2] The Bureau of Standards obtained a result of 0.020 per cent aluminum, and Electro Metallurgical Co., 0.022 per cent, when this standard was made.

Determination of Zirconium in Plain Carbon and Alloy Steels[1]

Thos. R. Cunningham and R. J. Price

UNION CARBIDE AND CARBON RESEARCH LABORATORIES, INC., LONG ISLAND CITY, N. Y.

ZIRCONIUM is separated from the elements enumerated below as $ZrHPO_4$, which is converted to ZrP_2O_7 on ignition. A determination may be completed on steels free from tungsten, tin, tantalum, or columbium in not over 2 hours. The exact determination of very small percentages of zirconiun in the presence of varying amounts of one or more of the elements titanium, aluminum, tungsten, molybdenum, chromium, vanadium, uranium, cobalt, nickel, copper, tin, arsenic, manganese, tantalum, columbium, and silicon, all of which are found in one type or another of plain carbon or alloy steel, is a somewhat difficult analytical problem. The method herein described is designed to be applicable to any commercial steel.

From 5 to 10 grams of the drillings are transferred to a 500-cc. covered beaker and dissolved in 40 to 60 cc. of hydrochloric acid (sp. gr. 1.19). When all action appears to have ceased from 8 to 15 cc. of Perhydrol (30 per cent hydrogen peroxide) are introduced to oxidize the iron, to break up any separated carbides, to oxidize tungsten, and to peroxidize the titanium. If the steel contains tungsten, a yellow precipitate of tungstic acid will be noticed at this point, in which case the procedure must be modified as described below. Titanium is not precipitated as phosphate when in the sexivalent state. The solution is diluted with warm water to 350 cc., treated with 8 to 10 grams of diammonium phosphate dissolved in 50 cc. of water, and stirred vigorously for several minutes. Some ashless paper pulp is introduced, and after allowing the solution to stand for one-half hour at a temperature of approximately 70° C. it is filtered on an 11-cm. paper. The precipitate and paper are washed 15 to 20 times with 2 per cent hydrochloric acid, ignited in porcelain at a low temperature to burn off the paper, and transferred to a 30-cc. platinum crucible. Two cubic centimeters of sulfuric acid (1 to 1) and 5 cc. of hydrofluoric acid (48 per cent) are added and the solution is evaporated to strong fumes of sulfur trioxide.

The sulfuric acid solution is transferred to a 150-cc. beaker, the crucible being rinsed with 5 cc. of hydrochloric acid (sp. gr. 1.19) and a little water, and added to the beaker. The solution is diluted with warm water to 75 cc., treated with 3 grams of diammonium phosphate dissolved in 25 cc. of water, stirred vigorously, and allowed to stand for one-half hour at a temperature of approximately 70° C. The solution is filtered on a 9-cm. paper containing some ashless paper pulp and the precipitate of $Zr(HPO_4)_2$ and paper washed 15 to 20 times with 2 per cent hydrochloric acid. The precipitate is ignited in platinum first at a low temperature to burn off the paper, and finally at 1000° C., cooled in a desiccator, and weighed. The weight of ZrP_2O_7 is multiplied by 34.23 and divided by the weight of sample taken to give the percentage of zirconium in the sample. For extreme accuracy the precipitate of ZrP_2O_7, which may be contaminated with small amounts of $Ti_2P_2O_9$, is fused with several grams of potassium pyrosulfate and the fusion dissolved in 40 cc. of 10 per cent sulfuric acid containing 5 cc. of 3 per cent hydrogen peroxide. The titanium is then determined by the hydrogen peroxide colorimetric method and the calculated weight of $Ti_2P_2O_9$ deducted from the weight of the precipitate of ZrP_2O_7. The weight of $Ti_2P_2O_9$ is obtained by multiplying the weight of titanium found by 3.16.

The ignited and weighed residue may not correspond exactly to the composition of ZrP_2O_7 (*1*) but it is believed to be very close to it, since the results obtained by the above described procedure agree almost exactly with those obtained by the cupferron method. By the latter procedure the zirconium is weighed as zirconium dioxide. This method should not be applied to the determination of large amounts of zirconium because the precipitate of $Zr(HPO_4)_2$ is somewhat gelatinous, which makes it rather difficult or almost impossible to wash out the excess of the precipitant completely.

In the case of chromium steels that do not dissolve completely in the hydrochloric acid–Perhydrol treatment, the ignited residue, instead of being treated with sulfuric acid and hydrofluoric acid to remove silica, is treated with 5 cc. of hydrofluoric acid (48 per cent), 3 cc. of nitric acid (sp. gr. 1.42), and 3 cc. of perchloric acid (60 per cent), and the solution evaporated to strong fumes of perchloric acid. The perchloric acid serves to break up chromium carbide and to oxidize the chromium to chromic acid which does no harm.

In the case of tungsten steels, after adding the Perhydrol, the solution should be boiled for about 5 minutes before diluting with warm water to 350 cc. and treating with the diammonium phosphate solution. After allowing the solution to stand for one-half hour at a temperature of about 70° C., it is filtered on an 11-cm. paper and the paper and precipitate washed well with 2 per cent hydrochloric acid, ignited in porcelain at a low temperature, and transferred to a 30- or 50-cc. platinum crucible. The residue is fused with about 10 grams of sodium carbonate and the melt is dissolved in hot water in a 250-cc. beaker. Some ashless paper pulp is added and the precipitate of sodium zirconate is filtered on a 9-cm. paper and washed thoroughly with 2 per cent ammonium nitrate solution to remove all sodium tungstate and sodium salts. The precipitate of sodium zirconate is ignited in the same platnium crucible previously used and fused with 1 to 2 grams of potassium pyrosulfate. The fusion is dissolved in 75 cc. of hot 5 per cent hydrochloric acid containing 5 cc. of 3 per cent hydrogen peroxide, and the zirconium precipitated with diammonium phosphate as previously described. The precipitate is allowed to stand one-half hour at a temperature of about 70° C., filtered on a 9-cm. paper, washed well with hot 2 per cent hydrochloric acid, and ignited in a weighed platinum crucible. The precipitate is treated with a few drops of sulfuric acid (1 to 1) and several centimeters of pure hydrofluoric acid (48 per cent), and any silica is expelled by evaporating the solution to the complete expulsion of the sulfuric acid. The crucible is heated at 1000° C., cooled in a desiccator, and weighed. The weight of ZrP_2O_7 is multiplied by 34.23 and divided by the weight of sample taken to give the percentage of zirconium in the sample.

Should the steel be known to contain tin, tantalum, or columbium, the phosphate precipitate is filtered, washed thoroughly with 2 per cent hydrochloric acid, ignited in porcelain, transferred to a platinum crucible, and in the case of tin, fused with sodium carbonate, or transferred to a

[1] Received October 16, 1930.

nickel crucible if tantalum or columbium are present and fused with several grams of potassium hydroxide. The melt is dissolved in water and the determination completed as described for tungsten steels.

Experimental Proof of Accuracy of Method

A number of experiments were carried out to obtain dependable data concerning the accuracy of the method. It is a well-known fact that unless hydrogen peroxide is added to peroxidize the titanium, it will be carried down with the zirconium phosphate precipitate, and for this reason alone, when extreme accuracy is desired, the final zirconium phosphate precipitate should be tested for titanium. The procedure consisted in salting a number of samples of plain carbon steels, a sample of Cr-W-V steel, and stainless steel of the 18 chromium–8 nickel variety known to be free of zirconium, with varying amounts of pure zirconium chloride. Five-, ten-, and twenty-gram samples, respectively, were used. The accurately measured aliquot portions of the standard solution of pure zirconium chloride were added to the weighed samples of steel, which were then dissolved and otherwise treated as given in the description of the method. The results obtained are given in the table.

Experiments to Test Accuracy of Method

Experiment	Kind of Steel	Steel Taken	Zirconium Added	Zirconium Found	Error
		Grams	*Gram*	*Gram*	*Gram*
1	Plain C	20	0.00101	0.00095	−0.00006
2	Plain C	20	0.00101	0.00102	+0.00001
3	Plain C	5	0.0025	0.0025	.....
4	Plain C	5	0.0025	0.0025	.....
5	Cr-W-V[a]	10	0.0006	0.00058	−0.00002
6	18 Cr-8 Ni	5	0.00133	0.00132	−0.00001

[a] Bureau of Standards standard sample 50A of high-speed steel. Two 5-gram portions were taken and the precipitates combined after making the sodium carbonate fusion to separate the tungsten.

Literature Cited

(1) Lundell and Knowles, *J. Am. Chem. Soc.*, **41**, 1801 (1919).

Rapid Colorimetric Method for Determination of Molybdenum in Plain Carbon and Alloy Steels[1]

Thos. R. Cunningham and H. L. Hamner

Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y.

An accurate colorimetric method for the determination of molybdenum in the presence of nickel, chromium, tungsten, and other elements, is given. It is best adapted to steels containing a maximum of 1 per cent molybdenum. However, good results have been obtained when the molybdenum content was as high as 2.5 per cent.

One-half gram or one gram of the sample (if the molybdenum is 0.10 per cent or less) is transferred to a 150-cc. covered beaker and treated with 25 cc. of sulfuric acid (1 to 4) at a temperature of approximately 60° C. When all action appears to have ceased, 3 cc. of Perhydrol (30 per cent hydrogen peroxide) are introduced and the liquid is boiled for several minutes. The solution is then filtered on a 9-cm. paper to remove carbon and the residue washed with water and discarded. The filtrate and washings are collected in a 250-cc. beaker and boiled down to a small volume to decompose completely the excess of Perhydrol. The Perhydrol destroys the hydrocarbons and partially reduces the molybdenum to a lower state; part of the molybdenum is oxidized by the air. In the case of plain carbon or alloy steels, or steels containing tungsten, the above filtering operation is omitted. One gram of tartaric or citric acid is added (to tungsten steels only) and the solution made slightly alkaline with 10 per cent sodium hydroxide and then acid with an excess of 10 cc. of sulfuric acid (1 to 1). The tartaric or citric acid serves to hold up the tungsten. If only a small amount of tungsten is present this treatment may be omitted.

The cold solution is transferred to a 250-cc. separatory funnel provided with a glass stopper, diluted to a volume of 100 cc. with cold water, and treated with 10 cc. of 5 per cent potassium thiocyanate solution. The stoppered flask and contents are shaken vigorously for several minutes, then treated with from 5 to 10 cc. of stannous chloride solution and again shaken vigorously for several minutes. The stannous chloride reduces the iron from the ferric to the ferrous condition and the molybdenum from the sexivalent to the quinquevalent or quadrivalent state. The potassium thiocyanate reacts with the reduced molybdenum to form a complex potassium-molybdenum thiocyanate, which imparts an amber to reddish brown color to the solution, depending upon its intensity.

The solution is cooled to approximately room temperature, 50 cc. of ether added, and the separatory funnel stoppered and shaken vigorously for 30 seconds and then allowed to stand until the liquid has separated into two distinct layers. The lower or acid layer, which will contain the greater part of any iron, chromium, nickel, or tungsten, is drawn off and discarded, and the upper or ethereal layer, which will contain practically all of the molybdenum, is then drawn off into a 50-cc. Camp comparison tube. The tube is stoppered with a soft cork to prevent evaporation of the ether and its contents are mixed thoroughly by manipulating the tube in the usual manner. After standing for several minutes it is ready for comparison with the standard.

Preparation of Standard for Comparison

With a little practice it is not difficult to estimate approximately the percentage of molybdenum in the sample. Twenty-five cubic centimeters of 8 per cent ferric sulfate solution are transferred to a 250-cc. separatory funnel and the standard molybdenum solution added from a buret. The solution is diluted with cold water to approximately 100 cc. and the development of the molybdenum color and extraction are completed as previously described. It is advisable to allow the molybdenum solution to stand in the comparison tube for several minutes before comparing with the standard, as the intensity of the color sometimes changes at first but remains stable thereafter for 7 days and even longer if kept in the dark when not in use.

The percentage of molybdenum in the sample is then determined by comparing the intensity of the color of the ethereal solution of potassium–molybdenum thiocyanate with that of the standard. The darker of the two solutions, the sample and the standard, is diluted carefully with ether

[1] Received October 16, 1930.

and mixed thoroughly until they match exactly. The amount of molybdenum per cubic centimeter in the standard is then figured and the calculation of the percentage of molybdenum in the sample is obtained by multiplying the weight of molybdenum in each cubic centimeter by the number of cubic centimeters, dividing by the weight of sample taken, and multiplying by 100. The following example illustrates the calculations involved: In comparing the standard with the sample, 15 cc. of the standard molybdenum solution (1 cc. = 0.0002 gram Mo) were used and diluted to 44 cc. with ether. Therefore,

$$15 \times 0.0002 = 0.0030 \text{ gram Mo}$$

$$\text{or } \frac{0.0030}{44} = 0.000068 \text{ gram Mo per cc.}$$

The sample was diluted to 36 cc.; hence,

$$36 \times 0.000068 = 0.00245 \text{ gram Mo in the 1-gram sample, or } 0.245 \text{ per cent Mo}$$

Solutions Required

Standard Molybdenum Solution—1 cc. = 0.0002 gram molybdenum. This solution is prepared by dissolving 0.430 gram of pure sodium molybdate in one liter of water containing 10 cc. of sulfuric acid (1 to 1), and mixing thoroughly. One hundred cubic centimeters of this solution are measured carefully by means of an accurately calibrated pipet into a 250-cc. beaker, 12 cc. of sulfuric acid (1 to 1) are added, and the solution is put through a Jones zinc reductor into 35 cc. of ferric phosphate solution and titrated with a standard solution of 0.05 N potassium permanganate (1 cc. = 0.0016 gram Mo).

A blank determination is run on the reductor and the solution of ferric phosphate (this usually amounts to about 0.2 cc.) by passing 100 cc. of 6 per cent sulfuric acid and 150 cc. of water (same amount as used in the analysis) through the reductor in exactly the same way as the molybdenum solution, and titrating the liquid with permanganate. The amount of 0.05 N potassium permanganate required to impart a pink tint to the liquid constitutes the blank to be deducted from the buret reading when standardizing the molybdenum solution.

Ferric Sulfate Solution (8 per cent)—Eighty grams of pure ferric sulfate are dissolved in one liter of 20 per cent sulfuric acid. The presence of iron is essential in the preparation of the standard since it has been determined by experiment that the ethereal solution of potassium-molybdenum thiocyanate is more comparable and also more stable than when it is omitted. The iron appears to have a catalytic effect.

Stannous Chloride Solution—Three hundred and fifty grams of stannous chloride are added to 200 cc. of hydrochloric acid (1 to 1) in a 500-cc. Erlenmeyer flask, the liquid boiled gently until the salt has almost dissolved, transferred to a liter bottle, and diluted with freshly boiled water to 1000 cc. A few pieces of metallic tin are introduced to prevent oxidation.

Ferric Phosphate Solution—Twenty-five grams of ferric sulfate are dissolved in 950 cc. of water containing 40 cc. of phosphoric acid (sp. gr. 1.72) and 10 cc. of sulfuric acid (sp. gr. 1.84).

The accuracy of the method is indicated by the tabulated results obtained on several samples of steel and on Bureau of Standards standard sample 61 of ferrovanadium by the volumetric and colorimetric methods.

Experiments to Test Accuracy of Method

Sample	Weight of Sample	Molybdenum Found Volumetric method	Molybdenum Found Colorimetric method
	Gram	%	%
Steel 1	0.6000	0.26	0.27
Steel 1	0.6000		0.27
Steel 1	0.6000		0.27
Steel 2	0.2500	0.33	0.34
Steel 2	0.5000		0.34
Steel 2	0.7500		0.33
Steel 2	1.000		0.33
Ferrovanadium standard 61[a]	0.5000	0.72	0.73

[a] The Bureau of Standards obtained a result of 0.72 per cent Mo by weighing as lead molybdate, and Electro Metallurgical Co., 0.72 per cent by the volumetric method when this standard was made in 1924.

The volumetric determinations were made on a 2-gram sample, the molybdenum being separated from the iron and vanadium with hydrogen sulfide by the present standard methods before passage of the sulfate solution through the Jones reductor.

Time Required for Analysis

	Minutes
Weighing of sample	½
Soln. of sample and boiling almost to fumes of sulfur trioxide	8
Cooling and making ether separation	10
Comparison with standard	2

The above time may be reduced after one has become accustomed to the method. It has been found that the intensity of the color remains stable for at least a week. Therefore, by making up a sufficient number of fresh standards the beginning of each week, say within a range of 0.02 per cent, it will only be necessary to dilute the unknown until the colors match. Of course the standards should all be diluted to the same volume. This will aid in reducing the time taken for making the comparison.

Lots of Bromine in the Ocean

Although practically all of the bromine produced in the United States has been obtained from salt brine deposits located in different states, the outstanding potential source of this chemical material is the sea, according to the United States Bureau of Mines. The rapidly increasing use of this material in motor fuel has attracted attention to the bromine content of the ocean. Bromine occurs in sea water to the extent of 60 to 70 p. p. m., except where fresh water from rivers may cause local dilution near the coast. Since the area of the oceans is 139,295,000 square miles—almost two and one-half times the area of the land—and since the depth averages 3 miles, sea water represents a virtually inexhaustible source of supply of any chemicals that can be commercially extracted therefrom. Experiments have demonstrated that this bromine actually is available, and the importance of this discovery is evidenced by the fact that only 1 cubic mile of sea water would supply for 392 years all the requirements of a plant producing 100,000 pounds of bromine per month.

Owing to the corrosive nature of the element it enters commerce largely in the form of its salt. Bromine is also sold as "mining salt," a mixture of sodium bromate and bromide. Solidified bromine has been used for laboratory work. Diatomaceous earth, formed with a suitable binder and burned into coherent sticks, is saturated with the liquid. These porous sticks absorb 50 to 75 per cent of bromine by weight.

Previous to about 1922 bromine was used principally in the form of sodium potassium or ammonium bromide in photography and for medicinal purposes. The photographic trade usually buys ammonium bromide of U. S. P. grade. "Mining salt" was formerly used in some quantity in the extraction of gold from its ores, but this use has apparently greatly declined. Bromine is used in the production of certain dyes, and liquid bromine as well as many of its compounds is employed in analytical chemistry. During the war some hand grenades and gas bombs were loaded with bromine or with organic bromine compounds.

The principal outlet for bromine at present, however, is as ethylene dibromide used in tetraethyl lead and antiknock compounds.

The world's bromine has come chiefly from Germany and the United States, being produced in the United States as early as 1846.

Problems in Estimation of Unsaturated Hydrocarbons in Gases

III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture[1,2]

H. S. Davis,[3] G. S. Crandall,[4] and W. E. Higbee, Jr.[4]

Massachusetts Institute of Technology, Cambridge, Mass.

It has been shown that aluminum chloride and certain other metallic salts prevent the quantitative titration of ethylene by the bromide-bromate method. It has further been established that oxygen prevents the quantitative titration of acetylene by the bromide-bromate method.

A standard procedure is developed by which ethylene and acetylene and some of their higher homologs are titrated quantitatively by bromide-bromate solution. This procedure is applied to the analysis of synthetic mixtures of gaseous olefins and acetylenes with encouraging results.

It is suggested that oxygen may be one of the principal causes of the irregularities found in halogen titrations of the acetylenes by other methods.

Propine and butine-1 are prepared and their boiling points determined in a vacuum-jacketed spiral column.

THE estimation of the unsaturated content of petroleum fractions by halogenation methods has been found to be subject to disconcerting variations. Further, the addition of the halogens to the acetylenes is incomplete. The causes for these variations have remained obscure. Two excellent reviews of this subject have recently been given (*9*, *12*), and the present paper deals with an experimental investigation of the factors affecting the completeness of the titration of unsaturated hydrocarbons by bromine, using the bromide-bromate method of Francis (*11*, *1*, *2*).

Experimental

Since this research dealt mainly with gaseous hydrocarbons, it was necessary to develop a special procedure for the titrations. The equipment required was a stout-walled reaction bottle fitted with a stopcock, described below, a machine to shake the reaction bottles set in a vertical position at a rate of 250 strokes per minute with a 4.5-cm. stroke, gas burets, Hempel gas pipets, 2 Geissler burets, and 1 Mohr buret fitted with a rubber tube 40 cm. long. The materials used were potassium bromide–bromate solution (approximately 0.5 *N*), sodium thiosulfate solution (about 0.1 *N*), 10 per cent sulfuric acid, bromine in potassium bromide solution, 33 per cent potassium hydroxide solution, potassium pyrogallate solution, and saturated potassium iodide solution.

The reaction bottle is a modification of the type used by Dobrjanski (*7*), and consists of a 300-cc. glass-stoppered bottle with a capillary stopcock sealed through the stopper. A short connecting tube of larger bore is sealed to the stopcock for attaching the apparatus to burets.

The general procedure for the titration of gaseous olefins is as follows: The bromide-bromate solution is measured into the reaction bottle which is then stoppered and evacuated by a water pump. A measured volume of the gas is drawn in without breaking the residual vacuum. Then dilute sulfuric acid is admitted slowly from the Mohr buret. Although the bromide-bromate solution is stable in neutral solution, it decomposes when acidified, liberating bromine. An equivalent quantity of acid is necessary to liberate the bromine as is shown by the following equation:

$$KBrO_3 + 5KBr + 3H_2SO_4 = 3K_2SO_4 + 3Br_2 + 3H_2O$$

Hence, by slow addition of the acid, the bromine is liberated slowly, and the rate can be so controlled that the bromine is taken up by the unsaturated compounds as fast as it is generated. In this manner, the concentration of the halogen is kept low so that substitution reactions are practically avoided. After the reaction is completed, saturated potassium iodide solution and considerable water are added. The vacuum is broken and the stopper removed. Then the iodine formed is titrated with standard thiosulfate solution. The mols of bromine absorbed by one mol of gas can easily be calculated.

After a large number of preliminary tests had been made on the olefins and acetylenes, the important fact was discovered that oxygen prevents the quantitative titration of acetylenes and probably of some diolefins. Accordingly, a procedure has been adopted which excludes oxygen as far as possible from the reaction flask.

Standard Procedure

The bromide-bromate solution required for the experiment is measured from the buret into the reaction bottle. The volume used should be only about 2 cc. in excess of the equivalent quantity, which must be determined by trial experiments or from a priori information about the approximate composition of the sample. The bottle is then evacuated by a water pump until the solution boils. If the tap water is not considerably cooler than room temperature, it may be necessary to heat the bottle with warm water. The gas sample is measured in a buret, is washed twice with potassium pyrogallate solution in a Hempel pipet (shaking one-half minute each time), and is then drawn into the buret and measured. The connecting tube of the evacuated bottle is filled with water to prevent the addition of air. It is then connected to the buret and the washed sample drawn into the bottle. The connecting tube is again filled with water and attached to the Mohr buret containing 10 per cent sulfuric acid. The rubber tube is about 40 cm. long to permit vigorous shaking of the bottle while it is attached to the buret. One cubic centimeter of the acid is added every half minute, the bottle being shaken vigorously between the additions. A volume of acid equal to the volume of bromide-bromate

[1] Received September 4, 1930. This paper contains results obtained in an investigation of the "Relative Rates of Reaction of the Olefins," listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Contribution No. 65 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology.

[3] Present address, Research Laboratories, Vacuum Oil Company, Paulsboro, N. J.

[4] Junior research fellows, Project No.19.

mixture taken is added, which is about a 200 per cent excess. When all the acid has been added, the buret is disconnected and the acid in the connecting tube is nearly all drawn in, care being taken that no air is admitted. The bottle is then shaken by the machine for 1 to $1^1/_4$ hours to complete the reaction. At the end of this time the bottle is removed and 3 to 5 cc. of saturated potassium iodide solution added; 20 cc. of water are also added before the vacuum is broken, the bottle is opened, and the solution diluted to from 100 to 150 cc. The iodine liberated is titrated to a colorless solution with standard thiosulfate solution. The total volume of unsaturated gas in a separate portion is determined by finding the fraction that is absorbed by bromine in potassium bromide solution.

Only a slight modification of this method is necessary for the titration of liquid or solid samples. The sample is sealed in a thin-walled glass capsule (*4*), weighed, and placed in the reaction bottle. After evacuating, the capsule is broken by shaking the bottle, the sulfuric acid is added, and the remainder of the analysis carried out as above.

Substances

PARAFFINS—Samples of gases compressed into small steel bottles were purchased. The degree of purity claimed for them was: methane, 92 per cent; ethane, 99 per cent; isobutane, 99 per cent; and normal butane, 99 per cent (*10*).

OLEFINS—The methods by which the olefins were prepared have already been described (*3*, *5*).

DIOLEFINS—*Propadiene* (*allene*), b. p. −32.8° to −31.3° C., was prepared by slowly dropping 2, 3-dibromopropene (Eastman Kodak Company) into boiling alcohol and zinc dust (*13*).

1, 3-Butadiene (*erythrene*), b. p. −2° to −1° C., was prepared by reducing erythrene tetrabromide with zinc dust in boiling alcohol solution. As Thiele has pointed out (*19*), it is necessary to add the tetrabromide slowly to the alcohol in order to obtain good yields. This requirement was met by placing the crystals in a test tube under the drip from a reflux condenser fitted to the flask, and under these conditions the yield of butadiene was 80 per cent of the theoretical. The erythrene tetrabromide, which had been prepared from cracked gases and recrystallized, was obtained through the kindness of V. Schneider.

ACETYLENES—Ordinary acetylene from a tank of the compressed gas was washed with water, with concentrated potassium hydroxide, with concentrated sulfuric acid, and was then stored over water. The sample gradually became contaminated with air.

Methylacetylene, b. p. −20° to −18° C. (compare −27.5° C., International Critical Tables, *14*), was prepared by slowly adding methyl iodide to sodium acetylide in liquid ammonia (*13*). The liquefied product was fractionated through a vacuum-jacketed spiral column.

Ethylacetylene was prepared in a similar manner, using ethyl iodide in place of methyl iodide, b. p. 6.8° to 8.5° C., (compare Picon's figure, 8° C., *18*). The value 18.5° C. given in the International Critical Tables (*17*) seems to be too high.

Samples of 1-heptine, 1-octine, 2-octine, and 4-nonine, were kindly supplied by R. L. Wakeman, who will describe their preparation elsewhere.

CYCLIC HYDROCARBONS—*Cyclopropane* (*trimethylene*) was prepared by dropping trimethylene bromide (Kahlbaum) into boiling isoamyl alcohol and zinc dust (*20*). The evolved gas was bubbled through 10 per cent potassium permanganate to remove olefins, liquefied, and fractionated. However, the product was not pure, probably because the permanganate treatment was not thorough enough. About 20 per cent by volume dissolved quickly in bromine water, and the remainder slowly; b. p. −28° to −27° C. (compare the value −34.4° C. given in the International Critical Tables, *15*).

The values obtained in various experiments are collected in Table I.

Table I—Results of Experiments with Various Substances

Substance	Procedure	Shaking Period	No. of Expts.	Mols Br_2 per 1 Mol Substance
		Hours		
	PARAFFINS[a]			
Methane	Standard	$2^1/_2$	1	0.01
Ethane	Standard	$1^1/_3$	1	0.00
Butane	Standard	$1^1/_4$	1	0.02
Isobutane	Standard	$1^1/_4$	1	0.07

[a] In this series the gases were not shaken with pyrogallate solution, but were washed with bromine in potassium bromide solution to remove any unsaturated compounds that were present.

Substance	Procedure	No. of Expts.	Mols Br_2 per 1 Mol Substance
	OLEFINS		
Ethylene	Standard	4	1.01
	With 7×10^{-3} mols O_2	2	0.95
	With 5×10^{-3} mols $AlCl_3$	1	0.16
	With 5×10^{-3} mols $Al_2(SO_4)_3$	2	0.46
	With 5×10^{-3} mols $Al_2(C_4H_4O_6)_3$	1	0.47
	With 5×10^{-3} mols $NiCl_2$	1	0.15
	With 5×10^{-3} mols $NiSO_4$	2	0.46
	With 5×10^{-3} mols HCl	1	1.02
Propene	Standard	1	1.01
	With 5×10^{-3} mols $Al_2(SO_4)_3$	1	1.00
1-Butene	Standard	1	1.07
	With 5×10^{-3} mols $AlCl_3$	1	1.04
2-Butene	With 5×10^{-3} mols $Al_2(SO_4)_3$	1	0.98
Isobutene	Standard	1	1.01
Isopropylethene	Standard	1	1.06
	DIOLEFINS		
Propadiene (allene)	Standard	1	1.94
1,3-Butadiene (erythrene)	Standard	1	2.00
	ACETYLENES[b]		
Acetylene (25.6% mixture in air)	Standard	1	1.89
Acetylene (25.6% mixture in air)	Standard (except not washed by pyrogallate)	1	1.47
Acetylene (1.48×10^{-3} mols)	1.36×10^{-3} mols O_2 added	1	1.64
Acetylene (1.42×10^{-3} mols)	3.23×10^{-3} mols O_2 added	1	1.49
Methyl acetylene	Standard	2	1.97
Ethyl acetylene	Standard	2	2.02
1-Heptine	Standard	1	2.01
1-Octine	Standard	2	1.74
2-Octine	Standard	1	2.05
4-Nonine	Standard	1	1.75

[b] Numerous preliminary experiments carried out before the role of oxygen was recognized indicated that aluminum, nickel, and mercuric salts aided the quantitative titration of acetylene, but since these same salts prevent the quantitative titration of ethylene they were not further investigated.

	CYCLIC HYDROCARBONS[c]		
Cyclopropane (trimethylene)	Standard	1	0.17
	With air present	1	0.16

[c] About 20 per cent of this sample dissolved rapidly in a solution of bromine and potassium bromide, the remainder very slowly, hence it must have contained some olefin (see preparation above).

Mixtures

A synthetic mixture (Experiment 3, Table II) containing 18.4 per cent of acetylene and 19.6 per cent of ethylene in air was titrated by the standard procedure (first washing with pyrogallate solution to remove oxygen). A 98.0-cc. sample (3.88×10^{-3} mols) containing 38 per cent (1.47×10^{-3} mols) of unsaturated gases, as shown by absorption in bromine water, reacted with 2.15×10^{-3} mols of bromine. From these figures the composition of the gas is easily calculated:

$$\% \text{ acetylene} = \frac{(2.15 - 1.47)}{3.88} \times 100 = 17.6\% \text{ (compare 18.4\% actual)}$$

$$\% \text{ ethylene} = \frac{[(2 \times 1.47) - 2.15]}{3.88} \times 100 = 20.4\% \text{ (compare 19.6\% actual)}$$

These results are in fair agreement with the actual composition of the sample. As pointed out below, the pyrogallate solu-

tion absorbs some of the unsaturated gases and more of the acetylenes than of the olefins. The collected results of the tests on synthetic mixtures are shown in Table II.

Table II—Analysis of Synthetic Mixtures by Standard Procedure

Experiment	Mixture	Olefin		Acetylene	
		Found	Actual	Found	Actual
		Mol %	*Mol %*	*Mol %*	*Mol %*
1	Ethylene, acetylene	64.0	62.5	25.7	28.1
2	Ethylene, acetylene	63.5	62.5	27.1	28.1
3	Ethylene, acetylene	20.4	19.6	17.6	18.4
4	Ethylene, acetylene	21.4	19.4	15.2	17.0
5	2-Butene, methyl acetylene	33.2	37.1	66.8	62.9

Dobrjanski (*7*) has used a similar method with success for the determination of erythrene in its mixtures with butenes, but his procedure is considerably more complicated.

Since acetylene is known to be more soluble in water than some of the gaseous olefins, being 8.6 times as soluble as ethylene at 25° to 30° C. (*17*), several semi-quantitative tests were carried out on the relative solubilities in pyrogallate reagent. Ethylene, propene, and 1-butene were absorbed at a rate of approximately 0.1 cc. per minute of contact when 100 cc. of gas were shaken well in a Hempel pipet filled with the reagent which was comparatively free from the olefins. On the other hand, acetylene was absorbed at a rate of 0.8 to 0.9 cc. per minute of contact under similar conditions.

Discussion

The most important facts which have been made clear by these experiments are that oxygen prevents the titration of acetylenes and that the titrations are largely quantitative in its absence. What may be a similar effect has been observed by Verhoogen (*21*) in brominations of the stereoisomers of α,β-dichlorethylene. She found that the fraction of the bromine disappearing after 23 hours varied with the gas in contact as follows: air, 0.14; nitrogen, 0.99; carbon dioxide, 0.998; and oxygen, 0.03.

It is possible that the explanation of these phenomena is that the intermediate dibromoethylenes absorb oxygen to give, after intramolecular rearrangement, bromacetyl bromides. Demole (*6*) showed that 1,1-dibromoethylene absorbs oxygen and Verhoogen (*21*) showed that the trans-form of α,β-dichlorethylene was greatly changed on standing 23 hours with oxygen. The resulting liquid fumed strongly in air, liberating hydrogen chloride and ketones. If this explanation is correct, it should be possible by careful measurements to detect the actual absorption of oxygen, and also to identify the products. On the other hand we may be dealing here with negative catalysis. Verhoogen concluded that in her experiments cited above, the rates of bromine addition were different.

The products from the bromination of the acetylenes in the absence of oxygen were heavy colorless liquids which sometimes crystallized. If, as seems probable, they are the corresponding tetrabromides, a way is open for the preparation of numerous tetrabromides which formerly have been difficult to synthesize.

The influence of oxygen in titrations by the Hanus and other methods will bear investigation. Thus Faragher, Gruse, and Garner (*8*) found that 1-heptine adds, from the Hanus reagent, only halogen corresponding to one double bond, whereas in our experiments both bonds were apparently saturated (see Table I).

Now that the disturbing influence of oxygen in these titrations has been made clear, the use of the bromide-bromate method for estimating unsaturated hydrocarbons can probably be considerably extended.

The error caused by the solubility of acetylene in aqueous solutions is serious. When in Experiment 1 of the acetylene section of Table I a correction is made for the solubility of the acetylene in the pyrogallate solution, the value 1.98 mols of bromine per mol of acetylene actually admitted to the reaction flask is obtained. Thus, it is obvious that for more accurate determinations of the unsaturated hydrocarbons in mixtures, it will be necessary either to use some other method for removing the oxygen, or to determine experimentally corrections for the solubilities of the gases present in the mixture.

Literature Cited

(1) Bacon, Ind. Eng. Chem., **20**, 970 (1928).
(2) Cortese, *Rec. trav. chim.*, **48**, 564 (1929).
(3) Davis, Ind. Eng. Chem., Anal. Ed., **1**, 61 (1929).
(4) Davis and Davis, Ind. Eng. Chem., **15**, 1057 (1923).
(5) Davis and Schuler, *J. Am. Chem. Soc.*, **52**, 721 (1930).
(6) Demole, *Ber.*, **11**, 316 (1878).
(7) Dobrjanski, *Neftyanoe Khozyaistvo*, **9**, 574–7 (1925). Translated by Paul N. Kogerman.
(8) Faragher, Gruse, and Garner, J. Ind. Eng. Chem., **13**, 1044 (1921).
(9) Faragher, Morrell, and Levine, *Ibid.*, Anal. Ed., **2**, 18 (1930).
(10) Fischer Scientific Co., Pittsburgh, Pa., "Laboratory," **2**, No. 3, 39.
(11) Francis, Ind. Eng. Chem., **18**, 821 (1926).
(12) Howes, *J. Inst. Petroleum Tech.*, **16**, 54–88 (1930).
(13) Hurd, Meinert, and Spence, *J. Am. Chem. Soc.*, **52**, 1138 (1930).
(14) International Critical Tables, Vol. I, p. 181 (1926).
(15) *Ibid.*, Vol. 1, p. 182 (1926).
(16) *Ibid.*, Vol. 1, p. 185 (1926).
(17) *Ibid.*, Vol. 111, p. 260 (1928).
(18) Picon, *Compt. rend.*, **158**, 1185 (1914).
(19) Thiele, *Ann.*, **308**, 339 (1899).
(20) Traust and Winkler, *J. prakt. Chem.*, (2) **104**, 37–43 (1922).
(21) Verhoogen, *Bull. soc. chim. Belg.*, **34**, 434–56 (1925).

Quantitative Determination of Pyrethrin I[1]

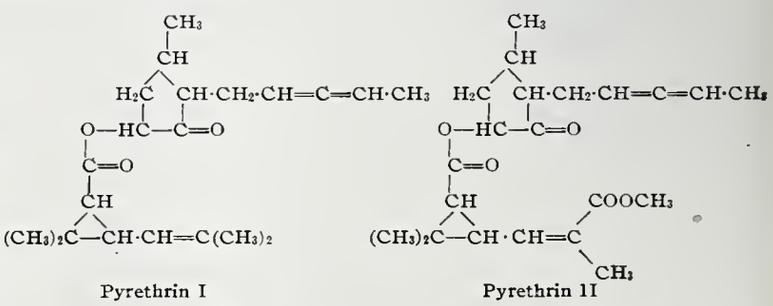
Ralph C. Vollmar

Chemical Laboratory, Standard Oil Company of California, Richmond, Calif.

THE classical researches of Staudinger and Ruzicka (*4*) established the constitution of the toxic principles present in pyrethrum flowers. They gave to the two active constituents the names pyrethrin I and pyrethrin II, and assigned to them the formulas given herewith.

Two methods for the quantitative determination of these constituents have been investigated by the author. It is the purpose of this paper to discuss the results which were obtained, and to report a series of experiments relating to the determination of these constituents in kerosene extract of pyrethrum flowers.

[1] Received October 6, 1930.



Pyrethrin I Pyrethrin II

A method based on the ability of the pyrethrins to reduce alkaline copper solution and to measure the amount re-

duced by comparison with a standard dextrose solution has been described by Gnadinger and Corl (*1*).

The acid method, originally published by Staudinger and Harder (*3*), has been simplified by Tattersfield, Hobson, and Gimingham (*5, 6*). Their short acid method for pyrethrin I is a determination which requires but a small sample and can be carried out in a short time. Briefly, 10 or 20 grams of flowers are extracted with petroleum ether in a Soxhlet extractor, the extract is hydrolyzed with alcoholic soda, is made acid and steam-distilled. The distillate is titrated with 0.02 *N* caustic soda.

Pyrethrin I has been shown to be more toxic to insects than pyrethrin II. Tattersfield, Hobson, and Gimingham found pyrethrin II to be but one-tenth the toxic strength of pyrethrin I, but in a more recent paper (*2*), Gnadinger and Corl maintain it is about 80 per cent as toxic. Inasmuch as the ratio of pyrethrin I to pyrethrin II is fairly constant, a method for the determination of pyrethrin I in flowers or an extract gives a good index of its toxic strength, regardless of the relative toxicity of the two constituents.

Sample 1, a sample of 1928 Dalmatian flowers, was run by both the short acid and the copper reduction methods with results that gave a good comparison between these two. The short acid method gave 0.31 per cent pyrethrin I, while the copper reduction method showed 0.75 per cent total pyrethrins.

The short acid method has been applied to a group of Dalmatian and California flowers, with the results given in Table I.

Table I—Analysis of Pyrethrum Flowers

Sample	Description	Pyrethrin I
		%
1	1928 Dalmatian, closed	0.31
36	1928 Dalmatian, closed	0.24
31	1928 Dalmatian, closed	0.23
61	1929 Dalmatian, closed	0.21
56	1929 California, open	0.20
63	Stems from sample 56	0.021

Experimental Work

Both these methods have been described only for samples of flower, stems, stalks, etc. A method for determining these constituents in a kerosene extract would be of value as a control test in the preparation of such extracts as are often used in commercial insect sprays. The short acid method was selected as the one best suited for developing into a control method.

No sample of pure pyrethrins or of an extract containing a known concentration of them was available to serve as a standard for experimental work, so a sample of concentrated kerosene extract was run several times by the method described for the flowers. A 5-cc. sample was used, along with 45 cc. of low boiling petroleum ether. A dilute extract was prepared by adding nineteen parts of kerosene to one part of concentrated extract, and this sample was run by the various methods described below. Table II shows the results on the original and dilute samples. For purposes of comparison, the results on the dilute sample have been calculated back to the original sample.

Table II—Pyrethrin I Content of Concentrated Extract

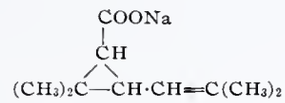
Method	Pyrethrin I
	Grams/liter
Original	3.6, 4.6, 4.8, 4.8, 5.4, 6.2 (av. 4.9)
Dilute samples:	
Original	1.8
Superheated steam	4.7, 5.1
Vacuum distillation	5.0, 5.1
Hydrolysis (2 extractions)	4.6, 4.9
Hydrolysis (3 extractions)	5.0

It will be noted that when the short acid method was applied directly to this dilute extract, using a 100-cc. sample, less than one-half the pyrethrin I is determined. This is probably due to the large volume of kerosene present in the distillation flask since 100 cc. more distillate collected gave but a small additional titration. A small volume of kerosene does not seem to affect the distillation.

The method which makes use of superheated steam is one in which 90 to 95 per cent of the kerosene is distilled, after hydrolysis of the pyrethrins, at a temperature of about 200° C. in a current of superheated steam. The results obtained were in good agreement with results from other methods, but no further work has been done on this one because the hydrolysis method gave equally good results, and is simpler.

In the vacuum distillation method, the same amount of kerosene was distilled at a pressure of from 2 to 3 mm. This method was not further developed on account of mechanical difficulties which render it unsatisfactory as a control method.

The hydrolysis method is based on the saponification of pyrethrin I to form the sodium salt of chrysanthemum monocarboxylic acid.



This removes the pyrethrin I from the kerosene layer, which may then be discarded. In order to keep the volume low and avoid transferring to a separatory funnel, the kerosene solution is extracted with two successive portions of alcoholic soda, and these extracts, along with a few cubic centimeters of kerosene, are then combined. Two extractions were found sufficient for complete removal of the pyrethrin I. When acid is added, the sodium salt breaks up, and the monocarboxylic acid is steam-distilled and titrated in the manner described by Tattersfield and Hobson (*6*).

Good checks were obtained using this method. Different operators running the same sample obtained results checking within 10 per cent of the total pyrethrin I, and an experienced operator can check himself within 5 per cent. Table III shows the results of a series of experiments in which ground Dalmatian flowers were steeped with kerosene at approximately 40° C. for 24 hours, after which the flowers were drained (but not dried), and analyses were run on both the wet flowers and the extract. The kerosene content of the wet flowers was about 30 per cent.

Table III—Comparison of Spent Flowers with Extracts

Sample	Pyrethrin I	
	Wet flowers	Extract
	%	%
37	0.067	0.064
40	0.040	0.041
42	0.018	0.024
44	0.015	0.012
46	0.008	0.009
64[a]	...	0.030

[a] Sample 64 was a mix of equal parts of samples 40 and 42.

The method which has been used to determine pyrethrin I in kerosene extracts follows. The presence of any ester of the type which is often used for an odorant will cause high results, hence this method is applicable only to extracts which are known to contain no foreign material. For the same reason it is not suitable for use in the qualitative determination of pyrethrins in an unknown extract.

Method

Solution Required—Sodium hydroxide in methanol, approximately 1 *N*. Fiftieth normal sodium hydroxide, 0.02 *N*. The strength of this solution should be checked occasionally. Sulfuric acid, 1 *N*. Petroleum ether, maximum boiling point 60° C.

Apparatus—For refluxing the sample and subsequent distillation, use a long-necked flask of 100 cc. capacity. The author used an ordinary distillation flask on which the side arm had been sealed.

PROCEDURE—Measure 100 cc. of extract into a long-necked flask of the type described above. (A smaller sample may be used if more than 0.05 per cent pyrethrin I is known to be present.) Add 5 cc. alcoholic soda solution and reflux for $1^1/_2$ to 2 hours, the bulb of the flask being immersed in a beaker of hot water. Shake occasionally. Remove from the beaker and pour off as much kerosene as can be decanted without disturbing the alcohol layer into another similar flask which contains a second 5 cc. portion of alcoholic soda. Reflux as before, and when completed, pour off the kerosene layer, rejecting it. A few cubic centimeters of kerosene will remain in each flask. Add to the second flask 11 cc. 1 *N* sulfuric acid, shake, and transfer to the first flask. Rinse the second flask with two 25-cc. portions of petroleum ether, and after transferring these washings to the first flask, confirm its acidity with phenolphthalein. Distil in a current of steam, using a long condenser cooled with ice water. Do not apply a flame to the distillation flask until all the petroleum ether has been distilled. Collect the petroleum ether and 50 cc. of water in a separatory funnel, then continue the distillation until an additional 50 cc. of distillate has been collected. Keep the volume low in the distillation flask, but do not allow it to go dry.

The titration is carried out in an Erlenmeyer flask to which has been added about 20 cc. carbon dioxide-free water, a few cubic centimeters of ethyl alcohol, and 1 cc. of phenolphthalein indicator. Add to this enough 0.02 *N* sodium hydroxide to give a definite pink color, usually one to two drops will be sufficient. Shake the contents of the separatory funnel vigorously and add the water layer to the second 50 cc. of distillate. Wash the petroleum ether layer with about 20 cc. of water, then add it to the titration flask. Titrate to a definite pink, shaking well and allowing the layers to separate after each addition. Extract the combined distillates with a second 50-cc. portion of petroleum ether, and add this to the titration flask. Continue the addition of caustic until the pink color is the same as it was originally. A blank determination should be run, using 100 cc. of kerosene, and the proper deduction should be made from each determination. This will usually be about 0.3 cc.

CALCULATIONS—From the molecular weight of 330, we get the relation, 1 cc. 0.02 *N* caustic = 0.0066 gram pyrethrin I.

Summary

The copper reduction and the short acid methods for determining active constituents in pyrethrum flowers are compared, and several samples of Dalmatian and California flowers run by the short acid method.

A series of experiments on the adaptation of the short acid method to a kerosene extract of pyrethrum are discussed.

A method for the quantitative estimation of pyrethrin I in a kerosene extract is described, along with a table showing pyrethrin I content of spent flowers and the extracts from these flowers.

Literature Cited

(1) Gnadinger and Corl, *J. Am. Chem. Soc.*, **51**, 3054 (1929); **52**, 680, 684 (1930).
(2) Gnadinger and Corl, *Ibid.*, **52**, 3300 (1930).
(3) Staudinger and Harder, *Ann. acad. sci. Fennicae*, [A] **29**, No. 18 (1927).
(4) Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 177, 450 (1924).
(5) Tattersfield and Hobson, *J. Agr. Sci.*, **19**, 433 (1929).
(6) Tattersfield, Hobson, and Gimingham, *Ibid.*, **19**, 266 (1929).

A Modified Balance for Approximate and Quick Weighing[1]

E. Karrer

B. F. GOODRICH CO., AKRON, OHIO

MANY cases arise when the time required to make a weighing must be kept at a minimum either because the weighings are approximate and large expenditure of time is unwarranted or because many things of the same kind are to be weighed. The economics of mass production demand that as little time as possible be spent upon each weighing. There is a very simple and inexpensive method for accomplishing this by modifying an ordinary beam balance as shown in Figure 1. A spring, *S*, is mounted directly under the beam, *H*, in which two adjustable studs, *A*, are inserted. These studs barely make contact with the spring, *S*, in the balanced condition. For example, the distance between the hardened ends of the studs and the spring may be 0.01 inch (0.25 mm.). The index, *B*, is lengthened and its position read by a scale, *C*. In making a weighing the scale pan, *G*, is depressed to the stop, *E*, and then is released quickly and carefully. If the weights on the two scale pans are equal the index will be deflected on its first swing to a point that may be marked zero on the scale, but if the weight on the scale pan, *F*, is slightly more than that on *G*, the index will not travel to that point. The distance traveled depends upon the difference in the weights on the pans. The modification described is best suited for comparing one article with another which is intended to be of the same weight and which is to be trimmed or adjusted to a given weight within certain tolerances. In such a case the standard article ("weigh-by") may be placed upon the pan *F*, and others, placed on pan *G*, be compared with this.

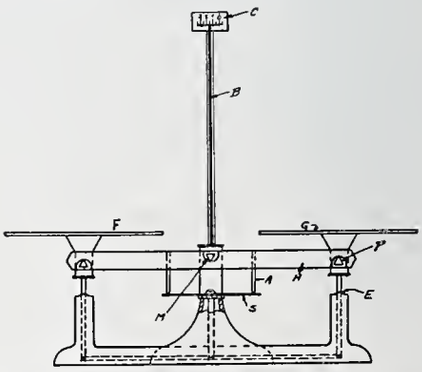


Figure 1—Balance Modified for Indicating Offweight on First Deflection

The scale *C* may be put in units of weight, of length, or of volume. For example, for comparison and control of pieces cut from ribbon or tubed stock, the scale *C* may be graduated in centimeters, indicating the length which must be cut from, or added to the piece in order to make its weight within tolerance limits equal to the weight of the standard. For

[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

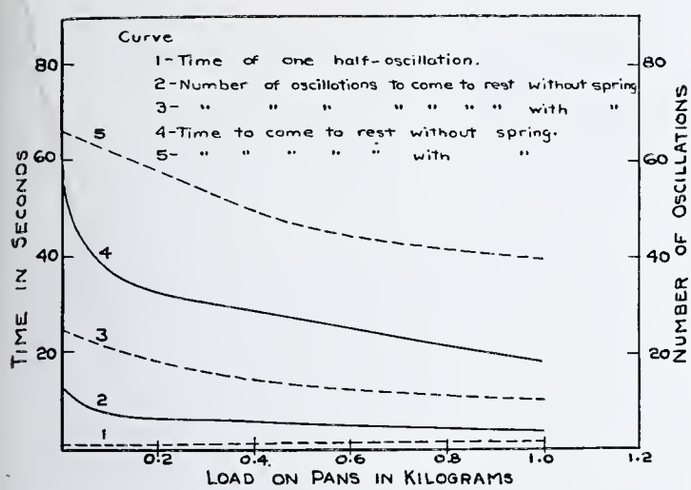


Figure 2—Time and Number of Oscillations before Coming to Rest

general purposes, the scale *C* graduated in terms of grams is more useful. It may even be graduated in terms of spoonfuls in case the materials being weighed are being meted out by approximate volumes, or it may indicate the number of cuts of a given size that are required to reduce the weight to within specified tolerances.

In a balance so equipped, it was found that an article could be laid upon the pan, the beam deflected, and the scale indicating the underweight or overweight read off in 2 seconds. By the ordinary method of weighing, this process consumed at least $2^1/_2$ seconds when the balances are read on the go—that is, when the state of balance was merely judged as to overweight or underweight by noting several deflections of the balance. An experienced operator can do this with fair accuracy at high speed. However, when the weight is obtained in 2 seconds, by the modified balance, exact information as to overweight and underweight is at hand, while when obtained by the ordinary method just mentioned, the overweight or underweight is only guessed at, so that at least one other trial on the balance is necessitated. This increases the time for one adjustment to at least 5 seconds.

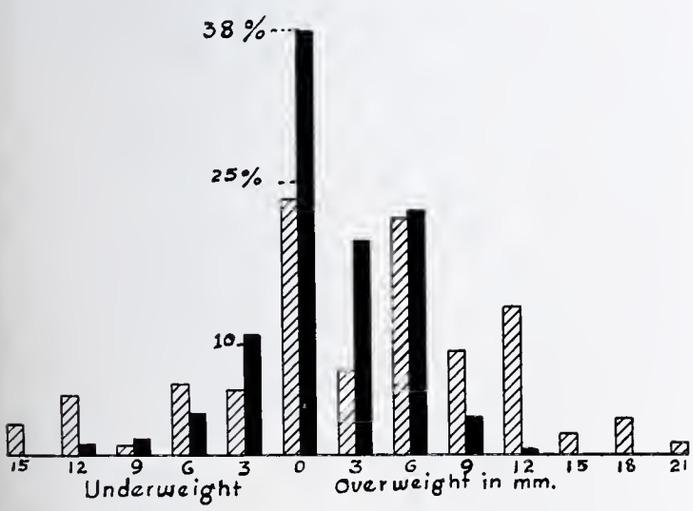


Figure 3—Distribution of Weight among Rubber Blocks before and after Adjustment with Balance

It was modified to indicate offweight quickly.

Figure 2 shows how certain characteristics of a balance change when it is equipped with a spring for quick weighing. From these curves a comparison may be made for different modes of weighing. In the method now discussed for the new balance, a weighing is made on the first half-oscillation of the index. The time (approximately 1 second) of the first half-oscillation is constant over a large range of loads (curve 1). When the condition of the balances is merely guessed at, one must observe theoretically at least $1^1/_2$ oscillations—making the time required approximately 3 seconds, but a much longer time is involved in actual practice, as just indicated.

Comparison with Unmodified Balance

To compare a balance modified for quick weighing with one unmodified and used in the ordinary way by estimation of the state of balance, a number of strips of rubber used in a routine process in the factory were weighed and adjusted by the two methods. The results are indicated in Figure 3, where the distribution of the samples according to weight is indicated by full columns for the balance equipped with the spring and used in the first deflection manner and by light columns for the customary method. Overweight and underweight are indicated on the abscissa in terms of centimeters of length. By the new method the number of products which are exact is over 50 per cent greater than the number by the usual method. In general, the distribution is changed in a very favorable manner—that is, the number showing small over- or underweight is generally much larger by the new

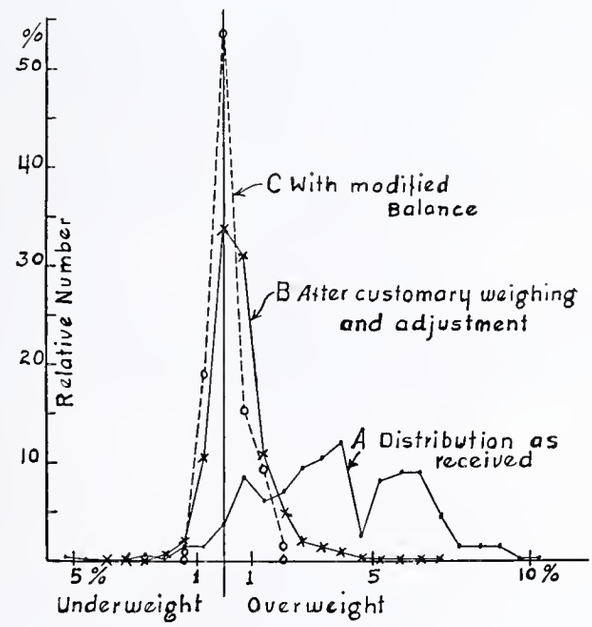


Figure 4—Distribution Curves for Overweighted Blocks before and after Adjustment with Ordinary and Modified Balances

method. The number which lie in the region of large underweight and large overweight are very much greater by the customary method than by the first deflection method with the modified balance. Further striking data are shown in Figure 4. In this case the distribution according to weight of rubber blocks as received is shown by curve *A*. After weighing and trimming by the usual method the distribution for several thousand blocks is represented by curve *B*. When the modified balance is used in the first deflection manner, curve *C* is obtained. The number of blocks weighing within 1 per cent of the standards has been greatly increased in the last case. There are practically no blocks differing by as much as 2 per cent from the standard. These weighings were made by one who had had much experience with these blocks in the factory. She had had no experience with the new method of weighing.

When the things to be checked by weighing have a cross section not favorable for adjustment by cutting off given lengths, then another method is to make certain that the blocks of material as delivered for checking are on an average slightly underweight. Then for adjustment, some small quantity of the material of standard shape may be added

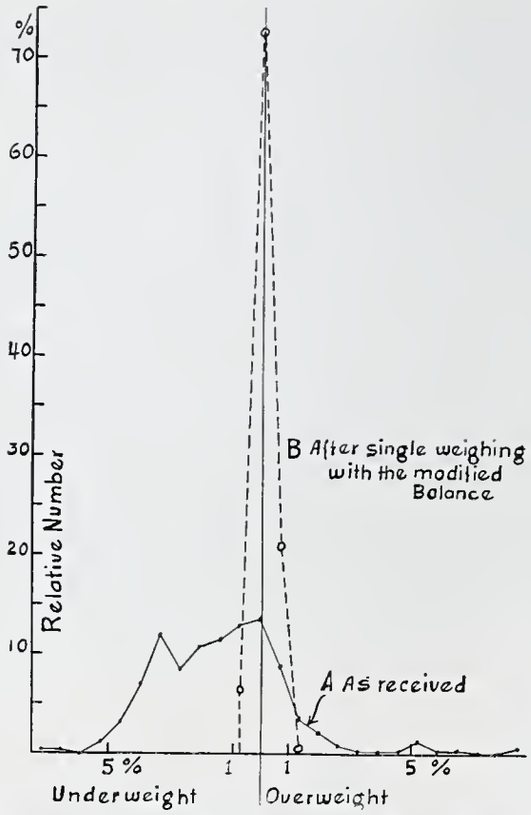


Figure 5—Distribution Curves after Adjustment with Modified Balance of Underweight Blocks

to bring the weight up to the comparison standard. The balance scale is now in terms of length, say of the stock to be added. An illustration of this is given in Figure 5, where the blocks as delivered for checking are represented by the distribution curve *A*. The resultant distribution after the adjustment has been made with a single weighing is represented by curve *B*.

The "weigh-by" in the case of Figures 4 and 5 was 1.7 kg. The variation in weight of blocks as delivered was so great that two springs were used to extend the offweight scale.

It is to be remembered that in making these weighings only a single laying upon the pan is necessitated by the modified balance with the single deflection method, whereas in the usual method, at least two, sometimes three or four weighing operations are required before the sample has been brought within limits. Not only is the distribution curve more favorable with the former method from the standpoint of elimination of waste, but it also consumes considerably less time. To make the weighings represented in Figure 4 required at least 10 per cent less time using the modified balance in the first deflection manner than when the customary method is employed. On another occasion 6 blocks per minute were adjusted by the new as compared with 5.04 by the customary method, or 19 per cent faster. If a comparison be made on the basis of the time required to bring about the same distribution, a much greater difference is brought out.

Apparatus for Continuous Leaching with Suction[1]

J. F. Fudge

Texas Agricultural Experiment Station, College Station, Texas

MANY laboratory methods require the continued leaching or washing of material. The addition of the leaching solution may become very tedious and time-consuming if a wash bottle or aspirator bottle be used. Schollenberger and Dreibelbis (*1*) describe an apparatus for continuous leaching. It is not, however, adopted to use with suction, and hence is unsuited to many laboratory operations. For example, in the determination of the base exchange capacity of a soil, as conducted in this laboratory, 10 grams of soil in a 35-cc. Gooch crucible are leached with 250 ml. of a neutral, normal solution of ammonium acetate. The excess ammonium acetate is then washed out with 95 per cent alcohol until the leachate gives no test with Nessler's solution. Suction is applied in order to reduce the time required for leaching and washing. Many soils leach very slowly, and without some self-operating apparatus a great deal of time may be lost in adding the leaching solution. For this reason, a number of different arrangements of apparatus were tried and the one described below finally selected. This has been found very satisfactory. The sizes and dimensions of the materials used are those adapted to the work described above. They may, of course, be varied at will to meet the requirements of other work.

The diagram gives all the essential characteristics of the apparatus. A few points should, however, be noted. The glass tubes are flush with the bottom of the stopper allowing for the complete removal of the measured volume of solution. The rubber tubing enables slight adjustment of the height of the glass tips. Tip *B* is drawn to a small hole in order to prevent splashing of the soil in the crucible. The tip of tip *B* should be at least $^1/_4$ inch below the tip of tip *A*. This difference is necessary in order to keep the solution flowing from tip *B* when tip *A* is in the air; if *A* and *B* are at the same height, both tubes fill up with solution and the flow stops. The entire apparatus is inverted after filling with the solution, and supported by a wooden support, with the bottom of both tips within and below the edge of the crucible.

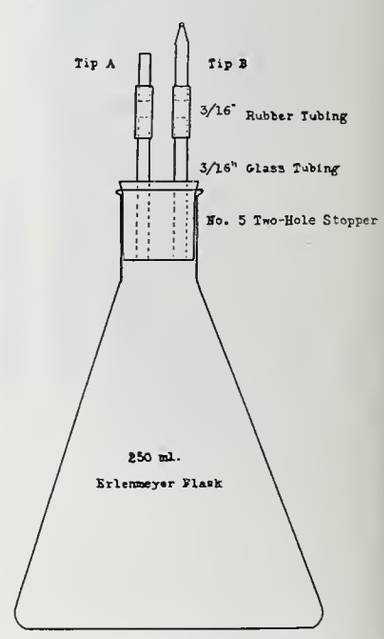


Figure 1—Diagram of Apparatus

[1] Received October 11, 1930. Technical Article 127 of the Texas Agricultural Experiment Station.

Literature Cited

(1) Schollenberger and Dreibelbis, *Soil Science*, **30**, 165 (1930).

Direct and Reverse Titration of Sulfuric Acid with Barium Hydroxide[1]

I. M. Kolthoff and E. B. Sandell

School of Chemistry, University of Minnesota, Minneapolis, Minn.

Potassium biphthalate (Bureau of Standards) is to be recommended for the standardization of barium hydroxide. Oxalic acid is less suitable for this purpose as the precipitate of barium oxalate carries down some bioxalate or oxalic acid. By titrating in hot solution this error is decreased to 0.1 per cent.

The titration of sulfuric acid with barium hydroxide cannot be used for precise work. The best results are obtained if the titration is performed at room temperature and if, after the first color change, the mixture is boiled and more base added until the color of the indicator persists for 15 to 30 seconds. After continued boiling for 5 minutes, the solution is cooled and the titration finished at room temperature. The accuracy obtained is 0.1 to 0.2 per cent. In the titration of a hot solution of sulfuric acid there is a greater occlusion of barium hydroxide.

In the precipitation of sulfuric acid with barium chloride, a small part of the acid is occluded. In precipitation at room temperature the occlusion is larger than at higher temperature.

The titration of barium hydroxide with sulfuric acid leads to erroneous results. A part of the base is occluded and a part adsorbed by the precipitate. The adsorbed base can be removed by boiling the mixture with a small excess of sulfuric acid; the error by occlusion is still about 1 per cent. The best results are obtained if the barium hydroxide is added to an excess of potassium sulfate at room temperature. The mixture is titrated at room temperature and, after the color change, boiled for 5 minutes with a small excess of sulfuric acid and titrated back at room temperature. The accuracy obtained is 0.0 to 0.2 per cent. If the potassium sulfate solution is added to the barium hydroxide, about 1 per cent of the base is occluded.

IT IS a well-known fact that barium sulfate precipitated from a sulfate or barium solution has a tendency to carry down other ions present in the solution. In the titration of sulfuric acid with barium hydroxide or in the reverse procedure, the possibility exists that either sulfuric acid or barium hydroxide may be co-precipitated. No accurate data on the accuracy of this titration are to be found in the literature. E. von Drather (*2*) concluded from rough experiments that in the titration of 0.2 *N* barium hydroxide with 0.2 *N* sulfuric acid, about 2 to 3 per cent too little base was found.

A special study of the deviations found in the titration of sulfuric acid with barium hydroxide and in the reverse procedure has been made. All titrations were made with weight burets, and precautions were taken against contamination by atmospheric carbon dioxide. About 0.2 *N* sulfuric acid and 0.2 *N* barium hydroxide solutions were prepared in carbon dioxide–free water and the normality of both determined by means of various standard substances. From the figures obtained, the normality ratio sulfuric acid to barium hydroxide was calculated and compared with the experimental ratio found by direct titration. As the calculated value is a little uncertain owing to errors made in the standardization of the acid and base, the same procedure was followed with hydrochloric acid and sodium hydroxide. In the latter case the experimental ratio can be determined without encountering the errors arising from the formation of a precipitate during the titration. Pure standard substances were prepared and tested for purity according to the directions given by one of the authors (*3*). The results have been corrected for the titration error, which was determined in an experimental way (for details compare Kolthoff, *3*). The results are given in Table I. The experimental and the calculated ratios agree within 0.02 to 0.03 per cent.

Calculated ratio of normality : sodium hydroxide to hydrochloric acid $= \frac{0.18914}{0.18084} = 1.0460$

Ratio found:	1.0462, 1.0462, 1.0463	(bromocresol green)
Ratio found:	1.0464, 1.0464	(phenolphthalein)
Average:	1.0463	

[1] Received September 26, 1930.

Table I—Standardization of Reagents

Standard Substance	Normality Found	Indicator
	Equivalents per 1000 grams	
	HYDROCHLORIC ACID	
Na_2CO_3 (product I)	0.18091, 0.18079, 0.18082, 0.18087, 0.18087; av. 0.18085	Bromocresol green
Na_2CO_3 (product II)	0.18083, 0.18085; av. 0.18084	Methyl orange
$KHCO_3$ (recryst. from H_2O)	0.18092, 0.18086, 0.18084; av. 0.18087	Bromocresol green
$KHCO_3$ (pptd. with alcohol)	0.18084, 0.18083, 0.18084; av. 0.18084	Bromocresol green
Borax I	0.18081, 0.18080, 0.18085; av. 0.18082	Bromocresol green
Borax I	0.18082, 0.18082; av. 0.18082	Methyl red
Borax II	0.18083, 0.18085; av. 0.18084	Bromocresol green
	Average normality: 0.18084	
	SODIUM HYDROXIDE	
Benzoic acid (B. S.)	0.18912, 0.18913, 0.18910; av. 0.18912	Phenolphthalein
Benzoic acid (Kahlbaum)	0.18918, 0.18913, 0.18911; av. 0.18914	Phenolphthalein
Oxalic acid	0.18917, 0.18915, 0.18918; av. 0.18917	Phenolphthalein
Oxalic acid (+$MgCl_2$)	(0.18935, 0.1894)	Bromocresol green
Potassium biphthalate	0.18909, 0.18912, 0.18915; av. 0.18912	Phenolphthalein
	Average normality: 0.18914	
	BARIUM HYDROXIDE	
Benzoic acid (B. S.)	0.19229, 0.19231, 0.19231, 0.19233; av. 0.19231	
Potassium biphthalate (*a*)	0.19221, 0.19222	
Potassium biphthalate (*b*)	0.19232, 0.19233, 0.19234; av. 0.19233	
Oxalic acid (*c*)	0.19300, 0.19305	
Oxalic acid (*d*)	0.19248, 0.19250, 0.19256	
	Average normality: 0.19232	

The sulfuric acid was standardized against the various standard substances used for the hydrochloric acid solution, an average normality of 0.20493 (equivalents per 1000 grams) being found. A few words may be said about the standardization of barium hydroxide with potassium biphthalate and oxalic acid, respectively. In a titration of an oxalic acid solution with barium hydroxide, the barium oxalate precipitating during the procedure carries down some oxalic acid or bioxalate. If the mixture is heated to boiling after the first color change of phenolphthalein, then cooled to room temperature and the titration continued until the color becomes pink again, the deviation is still 0.35 per cent from the theoretical value. By direct titration at room temperature Bruhns (*1*) found an error of 0.24 per cent, whereas

Schmitt (*4*) found a deviation of 0.3 per cent. According to the latter the titration of a hot solution of oxalic acid gives theoretical results. This statement was not confirmed in the present work, a deviation of 0.1 per cent from the theoretical value being found, if a hot solution of oxalic acid was titrated with barium hydroxide. Therefore, for work of high precision oxalic acid cannot be recommended for the standardization of barium hydroxide. Potassium biphthalate, on the other hand, is very useful, and gives theoretical results if a 0.05 *N* solution is titrated at a temperature of 40° to 50° C. At room temperature some barium phthalate may crystallize out at the end of the titration and carry down a trace of barium hydroxide. The error, however, is very small, amounting to about 0.05 per cent. In Table I the results of the standardization of barium hydroxide with benzoic acid, potassium biphthalate, and oxalic acid, respectively, are also reported. The titration of potassium biphthalate (*a*) was carried out at room temperature, the results given under (*b*) were obtained at 40° to 50° C., and the results reported for oxalic acid (*c*) were found by titrating at room temperature until a temporary end point was reached. The mixture was heated to boiling, cooled with protection of a soda-lime tube, and the titration finished with barium hydroxide (error 0.35 per cent). In experiment (*d*) the boiling solution of oxalic acid was titrated with barium hydroxide. After the end point had been reached, the color of the indicator did not change if the mixture was heated to boiling and cooled to room temperature.

Titration of Sulfuric Acid with Barium Hydroxide

The titration of sulfuric acid with barium hydroxide is given in Table II.

Calculated ratio of normality : sulfuric acid to barium hydroxide

$$= \frac{0.20493}{0.19223} = 1.0660$$

Table II—Titration of Sulfuric Acid with Barium Hydroxide

Calculated normality ratio $H_2SO_4 : Ba(OH)_2$, 1.066

Experiment	Addition	Temp. ° C.	No. of Titrations	Normality Ratio H_2SO_4: $Ba(OH)_2$ Found	Av. Deviation from Mean %	Av. Deviation from True Ratio %
1	.....	Room	4	1.067	0.1	+0.1
2*a*	.....	100	3	1.072	0.2	+0.6
2*b*	.....	100	3	1.070	0.1	+0.4
3*a*	0.5 *N* $BaCl_2$ added in excess to H_2SO_4 at room temp.	Room	2	1.057	0.0	−0.85
3*b*	0.5 *N* $BaCl_2$ added in excess to H_2SO_4 at room temp.	Room	2	1.057	0.05	−0.85
3*c*	0.5 *N* $BaCl_2$ added in excess to H_2SO_4 at 100° C.	100	2	1.062	0.0	−0.4
4	H_2SO_4 added to excess $BaCl_2$ at 100° C.	Room	2	1.062	0.1	−0.4
5	$Ba(NO_3)_2$ added to H_2SO_4 at 100° C.	Room	2	1.062	0.0	−0.4

Explanatory Remarks

Experiment 1. The end point obtained in the cold was not permanent. Therefore, the liquid was heated to boiling and barium hydroxide added until the mixture was slightly alkaline; the boiling was continued for 5 minutes and the titration then finished at room temperature.

Experiment 2*a*. Barium hydroxide was added rapidly to the hot sulfuric acid solution. When the end point had been reached (first tinge of pink) the mixture was boiled for 5 minutes; the pink color of phenolphthalein faded only slightly during the boiling. The titration was finished at room temperature.

Experiment 2*b*. In this case barium hydroxide was added very slowly to the hot sulfuric acid. End point obtained as in Experiment 2*a*.

Experiment 3*a*. Twenty per cent excess neutral 0.5 *N* barium chloride solution was added drop by drop to the sulfuric acid, and the titration made immediately after the precipitation; after the first color change the mixture was boiled for 5 minutes and the titration finished at room temperature.

Experiment 3*b*. After the precipitation of barium sulfate with barium chloride, the liquid was heated to boiling and kept at 100° C. for an hour, and titrated after standing overnight; the titration was made as in Experiment 3*a*.

Experiment 3*c*. Hot barium chloride was added drop by drop to hot sulfuric acid. Titration with barium hydroxide was made in hot solution; near the end point the liquid was boiled for a few minutes. The final end point was obtained at room temperature. If the precipitate was allowed to stand an hour at 100° C. and then titrated in the cold after standing overnight, practically the same results were obtained.

Experiment 4. Titration was made in hot solution; the final end point was obtained after cooling.

Experiment 5. The mixture was titrated after cooling to room temperature, the final end point obtained after boiling the liquid and cooling.

Titration of Barium Hydroxide with Sulfuric Acid

The titration of barium hydroxide with sulfuric acid is given in Table III.

Table III—Titration of Barium Hydroxide with Sulfuric Acid

Calculated normality ratio $H_2SO_4 : Ba(OH)_2$, 1.066

Experiment	Addition	Temp. ° C.	No. of Titrations	Normality Ratio	Av. Deviation from Mean %	Av. Deviation from True Ratio %
1*a*	.....	Room	3	1.084	0.3	+1.7
1*b*	.....	Room	2	1.076	0.15	+0.95
2*a*	.....	100	2	1.082	0.1	+1.5
2*b*	.....	100	3	1.075	0.1	+0.85
3*a*	$Ba(OH)_2$ added to excess K_2SO_4 at room temperature	Room	2	1.070	0.0	+0.4
3*b*	$Ba(OH)_2$ added to excess K_2SO_4 at room temperature	Room	3	1.064	0.2	−0.2
4*a*	$Ba(OH)_2$ added to excess K_2SO_4 at 100° C.	Room	3	1.083	0.3	+1.6
4*b*	$Ba(OH)_2$ added to excess K_2SO_4 at 100° C.	Room	3	1.066	0.1	0.0
5*a*	Excess K_2SO_4 added to $Ba(OH)_2$ at room temperature	Room	2	1.083	0.1	+1.6
5*b*	Excess K_2SO_4 added to $Ba(OH)_2$ at room temperature	Room	3	1.078	0.3	+1.1

Explanatory Remarks

Experiment 1*a*. The average normality ratio was obtained by taking the first color change in the cold as the end point. When the mixture was boiled the liquid became alkaline owing to slow liberation of co-precipitated barium hydroxide. Thus, in a particular titration the ratio found by taking the end point as the first disappearance of the pink color of phenolphthalein at room temperature was 1.087; after boiling 5 minutes, cooling, and adding acid to restore neutrality, the ratio became 1.085, and after another 5-minute period of boiling, 1.083, etc.

Experiment 1*b*. When the end point had been reached in the cold, about 1 gram of the standard sulfuric acid was added in excess and the mixture boiled for 10 minutes, then cooled, and the acid back-titrated with barium hydroxide.

Experiment 2*a*. After the color change in hot solution, the liquid was kept at the boiling point for 10 minutes, then cooled, and the titration finished at room temperature. The amount of barium hydroxide liberated by boiling for 10 minutes corresponded to about one drop of 0.2 *N* sulfuric acid.

Experiment 2*b*. After the color change at 100° C., about 1 gram of sulfuric acid was added in excess and the mixture boiled for 10 minutes; after cooling to room temperature the titration was finished with barium hydroxide.

Experiment 3*a*. The barium hydroxide was added drop by drop to 50 cc. of 0.5 *N* potassium sulfate solution and the mixture then titrated with sulfuric acid. Since the end point obtained in the cold was not permanent, the mixture was kept at 100° C. for 5 minutes, then cooled, and the titration finished at room temperature with sulfuric acid. The ratio thus obtained is given in Table III. After boiling the neutralized mixture for nearly an hour, the ratio 1.066 was obtained—nearly the theoretical value.

Experiment 3*b*. Barium hydroxide was added at room temperature to potassium sulfate as in Experiment 3*a*, but when a temporary end point had been obtained in the cold by titration with sulfuric acid, 1 gram of acid was added in excess and the liquid boiled for 10 minutes; the titration was finished as always at room temperature.

Experiment 4*a*. Fifty cc. of 0.2 *N* potassium sulfate were used. The barium hydroxide was added slowly and with constant shaking of the hot potassium sulfate solution. After cooling, the first end point obtained with sulfuric acid gave the ratio recorded in Table III. On boiling the mixture, barium hydroxide was slowly liberated. Thus, by boiling for 45 minutes and adding sulfuric acid whenever the liquid became alkaline, the value of the ratio finally obtained was 1.071.

Experiment 4*b*. As in Experiment 4*a*, but when the end point had been reached at room temperature, a gram of 0.2 *N* sulfuric acid was added in excess and the mixture boiled 10 minutes; the titration was then finished in the cold with barium hydroxide.

Experiment 5*a*. Fifty cc. of 0.5 *N* potassium sulfate at room temperature were slowly added to the cold barium hydroxide solution and the mixture titrated cold with sulfuric acid.

Experiment 5*b*. Same conditions as Experiment 5*a*, but when the end point was reached in the cold a slight excess of 0.2 *N* sulfuric acid was added and the mixture boiled for 10 minutes; the titration was finished, after cooling, with barium hydroxide.

Discussion of Results

Titration of Sulfuric Acid with Barium Hydroxide—Under no conditions are highly accurate results obtained; moreover, they are not so well reproducible as in ordinary acidimetric titrations where no precipitate is formed. Therefore, the titration is not suitable for work of precision. The best results are obtained if the acid is titrated at room temperature with barium hydroxide using phenolphthalein, phenol red, or methyl red as an indicator. After the first color change, the mixture is heated to boiling, more base is added until the color persists for 15 to 30 seconds. The boiling is continued for 5 minutes and the titration finished after cooling to room temperature (protection with soda-lime tube). It seems that a trace of barium hydroxide can be carried down by the barium sulfate (see Experiment 1, Table II); accuracy 0.1 to 0.2 per cent. For most practical work, these results are satisfactory.

If a hot solution of sulfuric acid is titrated, the deviation is much larger, amounting to about 0.6 per cent (Experiments 2*a* and 2*b*, Table II). Unexpectedly it is found that this error is due to co-precipitation of barium hydroxide with the barium sulfate although an acid solution is titrated. If the base is run in with great speed, a local excess is formed; better results may be expected if the barium hydroxide is added drop by drop with continuous shaking of the flask. That this is really the case is shown by Experiment 2*b*, though the deviation is still 0.4 per cent.

If the sulfuric acid is precipitated at room temperature with an excess of barium chloride, a co-precipitation of sulfuric acid takes place. The error is about 0.9 per cent (Experiment 3*a*). It was expected that heating the mixture after precipitation at room temperature might decrease the deviation as a result of growth of the small particles of the barium sulfate to larger crystals. However, as shown by Experiment 3*c*, Table II, heating had no effect.

If a hot solution of sulfuric acid is precipitated with a warm solution of barium chloride, the error due to occlusion is smaller though it still amounts to about 0.4 per cent.

It seems that two factors are responsible for the deviating results: adsorption and occlusion. Occluded sulfuric acid or barium hydroxide cannot be removed by boiling or by treatment with excess of base or of acid. The adsorbed acid can be removed fairly rapidly by boiling the mixture near the equivalence point for 5 minutes. By experiment, it could be shown that freshly precipitated barium sulfate adsorbs sulfuric acid. An excess of a hot solution of barium chloride was added to a warm solution of sulfuric acid. After 5 minutes' standing the mixture was filtered, and the precipitate washed with water until the reaction of the filtrate was neutral. The total filtrate was titrated with barium hydroxide. The ratio found was 1.037, thus indicating an adsorption of about 3 per cent sulfuric acid by the precipitate.

Titration of Barium Hydroxide with Sulfuric Acid—In the titration of a cold or hot solution of barium hydroxide with sulfuric acid a strong co-precipitation of the base by the precipitate occurs, the error amounting to about 2 per cent (Experiment 1*a*, Table III). This adsorbed base is only slowly removed by boiling the mixture near the equivalence point. It is better to add a small excess of sulfuric acid, boil for 5 minutes, and titrate back. The error then is still about 0.8 to 1 per cent and is caused by an occlusion of barium hydroxide by the precipitate (Experiment 1*b*).

From the Experiments 3*a* to 4*b* (Table III) it may be inferred that if barium hydroxide is added to an excess of neutral potassium sulfate solution, an adsorption of the base by the precipitate takes place. This adsorbed base can be removed by boiling the mixture near the equivalence point for a few minutes with a small excess of sulfuric acid. After back titration at room temperature the error is 0.0 to 0.2 per cent. By boiling the mixture near the equivalence point without adding an excess of acid, the adsorbed base is very slowly removed.

If the potassium sulfate solution is added to the barium hydroxide, an adsorption and occlusion of the base takes place. The error by occlusion is about 1 per cent.

Literature Cited

(1) Bruhns, G., *Z. anal. Chem.*, **55**, 23 (1916).
(2) Drather, E. von., *Chem.-Ztg.*, **52**, 518 (1928).
(3) Kolthoff, I. M., "Volumetric Analysis," Vol. II, translated by N. H. Furman, Wiley, 1929.
(4) Schmitt, K. O., *Z. anal. Chem.*, **71**, 284 (1927).

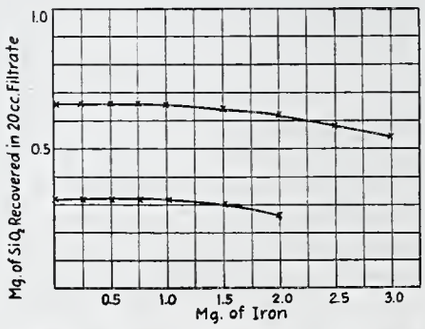
NOTES AND CORRESPONDENCE

Colorimetric Determination of Silica

Editor of Industrial and Engineering Chemistry:

In a recent issue [Ind. Eng. Chem., Anal. Ed., **2**, 276 (1930)] Thayer has made an exhaustive criticism of the well-known Diénert and Wandenbulcke [*Compt. rend.*, **176**, 1478 (1923)] method for the estimation of silica in natural waters. He has shown that in the presence of phosphate and iron the yellow color, which develops on adding ammonium molybdate and sulfuric acid to a dilute solution of silica, is considerably enhanced. In the case of sea water and many other natural waters, where phosphorus and iron are present only in minute amounts, the method of Diénert and Wandenbulcke can be used without modification. But where the waters contain considerable amounts of these elements, it is necessary to precipitate the phosphate and the iron and determine the silica in the filtrate. Thayer has shown that phosphate can be precipitated satisfactorily as calcium triphosphate at a weakly alkaline reaction but that in the presence of iron, in amounts of 25 mg. and more per liter, part of the silica is precipitated along with the phosphate and iron (Table IX). He has found, however, that iron can be precipitated in acetic acid solution as ferric phosphate without loss of silica, and the excess of phosphate then precipitated as calcium triphosphate.

In Thayer's paper there occurs the paragraph (p. 281): "After the writer had developed this method, his attention was called to the work of King, who determined silica in animal tissue by the Diénert and Wandenbulcke method after removing the phosphates with magnesia mixture. When no iron is present King's method should give quite satisfactory results, for there is little choice between the use of magnesium and calcium chloride. King states that the iron is precipitated along with the phosphate. He does not cite data to show that there is no loss of silica from



Effect of Iron on Recovery of Silica in Magnesia Precipitation of Phosphate from Silicate Solution

his solutions at the same time. The experiments cited above, however, make it seem highly probable that part of the silica is precipitated as ferric silicate during the precipitation of phosphate in King's procedure."

Thayer ignores the fact that I cited four analyses of lung and liver tissue where the results of the colorimetric estimations agreed very closely with those obtained by the ordinary macro-gravimetric method. It would seem that this close agreement of the results of the colorimetric method with those of the established method of gravimetric analysis of silica, is adequate experimental proof that there was no loss of silica during the precipitation of the phosphate and the iron which, of course, is invariably present in small amounts in animal tissue.

According to the reliable figures of Forbes and Swift [*J. Biol. Chem.*, **67**, 517 (1926)], who made a great number of careful analyses of a large variety of animal tissues, the largest amount of iron found in any tissue was 0.0188 per cent in the case of beef kidney with a moisture content of 78.67 per cent. This is equivalent to 0.088 per cent iron on the dry weight, or 0.88 mg. iron per gram of dry tissue.

King's method for the estimation of silica [*J. Biol. Chem.*, **80**, 25 (1928)] called for the use of 0.2 to 1.0 gram of dry tissue (0.25 gram was usually used), which was ashed, and the solution of the ash made to 30 cc. before adding the magnesia mixture. If, therefore, iron in quantities up to 0.88 mg. in 30 cc. of a silica phosphate solution is precipitated along with the phosphate on addition of magnesia mixture without loss of silica, it would seem highly improbable "that part of the silica is precipitated as ferric silicate during the precipitation of phosphate in King's procedure."

The following experiment shows that silica is not precipitated under these conditions unless more than 1 mg. of iron is present in the 30 cc. of solution. Since there is only a fraction of this amount of iron present in the amount of tissue used, there would seem to be no danger of loss of silica under the conditions specified in the method.

(1) Test solutions were prepared containing 1 mg. of silicon dioxide, 2 mg. of phosphorus (as $NH_4H_2PO_4$), and variable amounts of iron from 0 to 2 mg. (as $FeCl_3$), in 26 cc. To each were added 2 cc. of magnesia mixture and 2 cc. of 2.5 *N* ammonium hydroxide. After the mixtures had stood 5 minutes they were centrifuged clear and 20-cc. portions of each taken for the determination.

(2) Test solutions, consisting of 0.5 mg. of silicon dioxide, 1 mg. of phosphorus, different amounts of iron, and 1 cc. each of magnesia mixture and 2.5 *N* ammonium hydroxide, were made to 30 cc., filtered after 5 minutes, and colorimetric determinations made on 20 cc. of the filtrate.

The results obtained are illustrated in the accompanying graph. The presence of iron in quantities up to 1 mg. did not interfere with the recovery of the silica. Above that amount there was a partial precipitation of the silica which increased with larger quantities of iron.

EARL J. KING

DEPARTMENT OF MEDICAL RESEARCH
UNIVERSITY OF TORONTO
TORONTO, CANADA
September 22, 1930

. . . . . .

Editor of Industrial and Engineering Chemistry:

I regret that Mr. King apparently thinks I have implied a doubt as to the validity of his experimental data concerning the determination of silica in animal tissues, for it was hardly my intention so to do. It is obvious, I believe, from the comparison of colorimetric and gravimetric analyses cited by King in his original paper [*J. Biol. Chem.*, **80**, 25 (1928)], that his method of precipitating phosphates with magnesia mixture makes possible the satisfactory determination of silica in animal tissues, a point to which I will return later.

Neither was it my intention to reject the method as entirely unworthy of further attempts to develop it. Indeed, as compared with my calcium chloride solution, magnesia mixture has the advantage of being a standard reagent; and King's method, if it will work under all conditions, has the advantage of carrying out the precipitation of both iron and phosphates in one operation. It is with reference to the last point that I did, and still do, consider the method inadequately tested, as I shall try to point out.

Let us examine the results of the two experiments King cites in his letter with respect to the most extreme conditions which they represent. Experiment 2 shows that 1 (0.67?) mg. of iron in the presence of 0.67 mg. of phosphorus did not interfere with the determination of silica up to 0.33 mg. in 20 cc. of solution. Assuming that the iron will be precipitated as ferric phosphate or ferric silicate, there were present in the experimental solutions five equivalent weights of iron, six of phosphorus, and one of silica. In other words there was a slight excess of phosphorus over iron, and six times as much phosphate as silicate. The same ratio of constituents was used in both experiments; therefore the experiments give no information regarding the precipitation of silica as iron silicate when the proportion of phosphorus to silica is smaller. They do show that when the amount of iron is increased, there is a loss of silica. I believe that the worker who wishes to use the method would do well to assure himself more fully in regard to the influence of the ratio of phosphorus to silica and iron on the determination of silica.

It may safely be assumed, however, that there will be an excess of phosphorus over iron when animal tissue is the object of study, for the human body (if it be considered a fair example of mammalian bodies) contains, according to Lotka ["Elements of Physical Biology," p. 197], an average of 1.14 per cent phosphorus as against 0.01 per cent iron. Although the ratio is reduced to 0.4 per cent phosphorus [Forbes and Keith, Ohio Agr. Exptl. Sta., *Tech. Bull.* **5**, 141 (1914)] to nearly 0.02 per cent iron [Forbes and Swift, *J. Biol. Chem.*, **67**, 517 (1926)] in the case of beef kidney, there is still about 35 times as much phosphorus as iron.

LEWIS A. THAYER

DEPARTMENT OF BOTANY
STANFORD UNIVERSITY, CALIF.
October 22, 1930

Proceedings of Wood Painting Conference

The Forest Products Laboratory, Madison, Wis., has issued in a mimeographed volume a report of the proceedings of the Wood Painting Conference held at Madison September 13 and 14, 1929. This includes a complete set of formal papers and prepared discussion, as well as notes on extemporaneous discussion.

Analytical Industrial and Engineering Chemistry Edition

Published by the American Chemical Society

Volume 3 APRIL 15, 1931 Number 2

Determination of Carbon in Sewage and Industrial Wastes[1]

F. W. Mohlman and G. P. Edwards

The Sanitary District of Chicago, Chicago, Ill.

A modified chromic acid method for the determination of carbon in sewage and trade waste has been studied. The determination, which can be completed in about 3 hours, gives an accurate estimation of the strength of sewage or waste. This is particularly desirable for sewages or wastes high in carbon but low in nitrogen. There is a constant ratio between the organic carbon and the 5-day oxygen demand in the sewage and wastes used, supporting the theory that the first stage of the oxygen-demand curve is a carbon oxidation. There seems to be no relationship between the total carbon and the oxygen demand or between the total nitrogen and the oxygen demand.

IN VIEW of the fundamental importance of carbon compounds in all problems of sewage treatment and disposal, it is unfortunate that we have not had a satisfactory method for routine determination of carbon in sewage and industrial wastes. The ease and accuracy of the Kjeldahl method has made it possible to accumulate a large amount of information concerning the nitrogen compounds in sewage and wastes, but the only determinations we have had which are supposed to approximate the carbonaceous matter are the oxygen-consumed determination and the first stage of the B. O. D. test. It is, of course, true that neither of these is an actual determination of total organic carbon, for they include other oxidizable substances such as sulfur, hydrogen, and inorganic reducing compounds. Notwithstanding this lack of a method for determining carbon, it has long been known that in the oxidation of sewage the carbon compounds are of more importance than the nitrogen compounds. The large amount of nitrogen in urea has no appreciable demand for oxygen until hydrolyzed to ammonia. The nitrogen in ammonia is oxidized only slowly. It is therefore our belief that if a satisfactory method for carbon could be perfected the results would be correlated more closely with the actual oxygen requirements of the sewage than any correlation possible between the nitrogen and oxygen requirements.

Our attention was directed a year ago to some recent work on carbon determinations by Friedemann and Kendall (*2*). Their work applied to materials of biochemical importance, such as, for example, urine, blood, tissues, and bacterial culture media. In their work they found that the usual difficulty encountered in obtaining complete oxidation by chromic acid was caused by the presence of an excess of water in the sample. They demonstrated that the effect of large amounts of water could be compensated for by the use of larger amounts of sulfuric acid, and they show results of oxidation approaching 100 per cent of the theoretical amount. This work indicated to us that we might modify their apparatus and procedure for use in sewage work.

Methods of Carbon Determination

Carbon has usually been determined either by the dry combustion method or by the wet combustion method, using chromic acid. In the dry method the sample must be evaporated to dryness, which is impracticable with large volumes of liquid, the residue from which must be transferred from the evaporating dish to the combustion boat. Not only is there this difficulty but the carbon as determined will include carbonates. These unsatisfactory conditions and the time required and difficulty of the method have prevented its use.

The chromic acid oxidation method has had occasional study but results have usually been found to be low, and also difficulty has been encountered owing to liberation of sulfur trioxide and free chlorine. In the earlier work Schollenberger (*3*) showed that the sulfur trioxide fumes could be reduced by partial substitution of phosphoric for sulfuric acid. White and Holben (*4*) absorbed acid fumes in a U-tube filled with coarse glass wool drenched with 98.3 per cent sulfuric acid. Friedemann and Kendall demonstrated the importance of high concentration of acid. In our work we have added another precaution in absorbing in acid potassium iodide any free chlorine which may be liberated.

By taking advantage of these various improvements and suggestions we have developed apparatus and technic which seem to give promise of a method of practical value for the determination of carbon in sewage and industrial wastes.

Description of Method

The apparatus consists of a reaction flask, a Geissler tube for absorbing free chlorine, and an absorbing system for carbon dioxide. The oxidizing agents consist of chromic, sulfuric, and phosphoric acid, as recommended by Schollenberger. The carbon dioxide resulting from the reaction is absorbed by 0.1 *N* barium hydroxide, forming barium carbon-

[1] Received November 19, 1930. Presented before the Division of Water, Sewage, and Sanitation at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

ate which is insoluble. The excess barium hydroxide is titrated with 0.1 N hydrochloric acid, using phenolphthalein as the indicator. Care must be taken during the titration to add acid slowly, with shaking, so that acid concentration will not be large enough locally to dissolve the precipitate.

Apparatus—A sketch of the apparatus is shown in Figure 1. Three tubes pass through the ground-glass stopper of the 300-cc. Kjeldahl flask, A, which is fitted with a condenser on the outside of the neck. Tube B, attached to the separatory funnel, permits the addition of the oxidizing agents. Air, free from carbon dioxide, is drawn into the flask through tube C. Tube D leads from the Kjeldahl flask through the Geissler bulb, E, to the 300-cc. Erlenmeyer flask F. The absorption tower, G, containing glass beads which are held in place by a perforated porcelain plate, is connected to the Erlenmeyer flask. The tower is joined to the vacuum pump by the rubber tube with the clamp H, which regulates the flow of air through the apparatus.

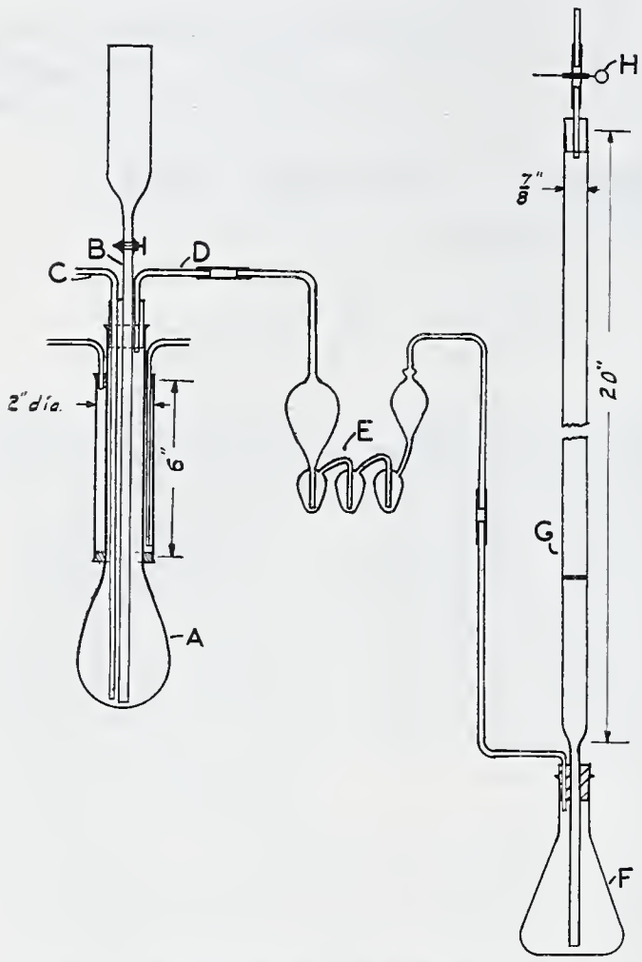


Figure 1—Apparatus for the Determination of Carbon in Sewage and Industrial Wastes

The vacuum pump draws carbon dioxide-free air through tube C into flask A. This air, with the carbon dioxide formed during the reaction, is drawn by way of tube D through the Geissler bulb, E. The Geissler bulb contains a saturated solution of potassium iodide, acidified with sulfuric acid to remove free chlorine liberated during the digestion. Then the air containing the carbon dioxide passes through flask F and the absorption tower which contains a definite volume of a standard solution of barium hydroxide. The carbon dioxide is absorbed by the barium hydroxide during the passage of the gas through the tower.

The absorption tower is large enough to hold 75 cc. of barium hydroxide during operation. Apparatus of this size is best for carbon determinations of industrial wastes with high carbon content.

Another set of apparatus used consists of a 500-cc. Kjeldahl flask with an absorption tower to hold 50 cc. of barium hydroxide. This size is more satisfactory for sewages and effluents containing small amounts of carbon.

Air freed from carbon dioxide is obtained from a 4-foot (1.22-meter) glass tube, one inch (2.54 cm.) in diameter, filled with moistened soda lime of about equal proportions of 4 and 8 mesh.

Reagents—(1) Chromic acid: 340 grams of chromic acid (CrO_3) are dissolved in 400 cc. of hot carbon dioxide-free water and made up to one liter with 85 per cent phosphoric acid. (2) Sulfuric-phosphoric acid: equal volumes of concentrated sulfuric acid and 85 per cent phosphoric acid. (3) 0.1 N barium hydroxide. (4) 0.1 N hydrochloric acid.

Procedure—A sample containing 10 to 30 mg. of carbon is placed in the Kjeldahl flask and the flask connected to the apparatus. Then 75 cc. of standard barium hydroxide are added to the Erlenmeyer flask and the vacuum is turned on so that air passes through the tower at the rate of 100 to 200 bubbles per minute. Next, 10 cc. of chromic acid and 50 cc. of the phosphoric-sulfuric acid mixture are added through the separatory funnel. As recommended by Friedemann and Kendall, 2 cc. of concentrated sulfuric acid are added for each cubic centimeter of water present in the sample. The contents of the flask are gently heated until the mixture boils. Gentle boiling is continued for 2 hours. At the end of the digestion, the flame is removed and the vacuum turned off. The stopper at the top of the absorption tower is removed and the tower is washed with about 150 cc. of carbon dioxide-free water. The flask is removed and the excess barium hydroxide is titrated with the standard hydrochloric acid solution to obtain the value for total carbon.

Blanks to correct for carbon dioxide in the apparatus and the reagents, and also for the carbon dioxide absorbed during the titration, should be run frequently.

Table I—Carbon Determination in Pure Compounds

Sample	Theoretical Carbon	Determined Carbon	Recovery
	Gram	*Gram*	%
Potassium acid phthalate	0.0147	0.0153	104
	0.0147	0.0144	98
	0.0147	0.0147	100
	0.0147	0.0146	100
Sucrose	0.0144	0.0143	99.3
	0.0144	0.0146	101.0
Asparagine	0.0096	0.00956	99.6
	0.0120	0.01186	99.0
	0.0120	0.01199	100
Sodium oleate	0.0157	0.01527	97.3
	0.0157	0.01497	95.5
	0.0157	0.01529	97.3
	0.0157	0.01545	98.0
Filter paper	0.01344	0.01335	99.5
	0.01384	0.01335	96.5

The free and combined carbon dioxide must be deducted from the total carbon in order to obtain the organic carbon. This may be done by first determining the carbon dioxide and then the organic carbon on the same sample, as follows: Another sample from the same source is placed in the Kjeldahl flask, the standard barium hydroxide added to the Erlenmeyer flask, and the apparatus connected. Two or three drops of the concentrated sulfuric acid are added through the separatory funnel and the contents of the Kjeldahl flask are slowly warmed. The sample is kept warm for an hour. The excess barium hydroxide, when titrated with hydrochloric acid, gives the amount of carbon dioxide and carbonate in the sample. A high concentration of acid and continued boiling may break down some of the organic matter, giving higher carbon dioxide results and correspondingly lower organic carbon, but it is probable that the carbon dioxide liberated in this way is small in comparison with total

Table II—Raw Sewage from North Side Treatment Works

Sample	Carbon			Total Nitrogen	5-Day B. O. D 20° C.	Organic Carbon / Total Nitrogen	Organic Carbon / B. O. D.	Total Nitrogen / B. O. D.
	Total	Organic	Free CO_2 plus carbonate					
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			
1	100.8 96.6[a]	57.0[a] 52.8	43.8	11.2	74	4.9	0.74	0.151
2	100.8 94.4[a]	57.6[a] 51.2	43.2	14.8	98	3.6	0.55	0.151
3	80.7 72.3[a]	37.2[a] 28.8	43.5	11.2	75	3.0	0.44	0.151
4	116.8 116.1[a]	56.5[a] 55.8	60.3	15.6	84	3.6	0.66	0.186
5	182.4 198.9[a]	62.3[a] 78.2	120.3	14.4	185	4.9	0.38	0.078
6	121.2 117.6[a]	70.2[a] 66.6	51.0	12.0	133	5.6	0.51	0.090
7	88.2 92.6[a]	27.4[a] 31.8	60.8	12.4	60	2.4	0.50	0.206
8	110.5 99.7[a]	59.7[a] 48.9	50.8	14.8	100	3.0	0.54	0.148
9	148.2 151.5[a]	90.0[a] 94.2	57.3	18.0	140	5.1	0.64	0.128
Av.	116.0	57.0	59.0	13.8	105	4.0	0.55	0.143

[a] Calculated.

Table III—Activated Sludge Effluent, North Side Treatment Works

Sample	Carbon			Total Nitrogen	5-Day B. O. D. 20° C.	Organic Carbon / Total Nitrogen	Organic Carbon / B. O. D.	Total Nitrogen / B. O. D.
	Total	Organic	Free CO_2 plus carbonate					
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			
1	58.5 59.6[a]	10.3[a] 11.4	48.2	1.60	2.0	6.7	5.4	0.800
2	49.8 50.2[a]	11.6[a] 12.0	38.2	0.80	3.0	14.5	3.9	0.266
3	60.9 60.9[a]	20.6[a] 20.6	40.3	1.04	6.0	19.8	3.4	0.173
4	60.0 61.6[a]	14.2[a] 15.8	45.8	2.60	3.0	5.8	5.0	0.868
5	54.4 53.6[a]	15.8[a] 15.0	38.6	0.88	3.4	17.5	4.5	0.259
6	52.2 54.0[a]	10.0[a] 12.0	42.0	0.88	2.8	12.6	3.9	0.314
7	52.2 55.0[a]	14.4[a] 17.2	37.8	1.68	5.7	9.4	2.8	0.294
8	47.5 49.7[a]	7.3[a] 9.5	40.2	1.00	2.3	8.4	3.6	0.435
Av.	55.0	13.6	41.4	1.31	3.5	11.8	4.1	0.426

[a] Calculated.

carbon, and that most of it may come from the carboxyl group (COOH), therefore not requiring oxygen for oxidation.

The acidified sample from which the carbon dioxide, free and combined as carbonate, has been removed is treated with chromic, sulfuric, and phosphoric acid as described above, and the organic carbon is determined. The sum of the carbon dioxide and the organic carbon should, of course, equal the total carbon, as originally determined.

Although a large quantity of sulfuric acid is necessary in the digestion of the large sample required when the carbon is low, it is the same amount recommended by Bauer and Deiss (*1*) for use in iron and steel analysis in the Corleis apparatus. They also recommend a 3-hour digestion period.

Results

Pure Compounds—The carbon was determined in a few pure compounds, such as a soap, an amino acid, a carbohydrate, and an aromatic compound. Table I shows that the determined values were very close to the theoretical ones. The sodium oleate seemed to contain some impurities, as it was partially insoluble in alcohol. These analyses were made on dilute solutions (0.01 *M*) of the compounds in the manner mentioned above for total carbon. The samples were boiled for 2 hours.

Friedemann and Kendall, working with smaller volumes of more concentrated solutions, found that the digestion of easily oxidizable substances, such as sugars, was complete in 30 minutes. Proteins required a longer digestion period, and substances difficult to oxidize, such as fats, required an hour. Certain compounds, such as stearic acid and carbazole, tended to creep upward and stick on the side and neck of the flask, giving low results.

The large volume of sample required in our analyses seemed to make necessary a longer digestion period. Digestion was complete in 2 hours.

Sewage and Effluents—Table II gives the results of analyses of nine samples of raw sewage obtained from the North Side Treatment Works, a sewage mainly of domestic origin. As mentioned before, the total carbon values were obtained from two determinations, the upper figure being the total carbon as determined, and the lower one the sum of the carbon-dioxide carbon and the organic carbon. The upper values for organic carbon are calculated by subtracting the carbon dioxide from the total carbon and the lower

Table IV—Wastes from J. Greenebaum Tanning Company

Sample	Carbon			Total Nitrogen	5-Day B. O. D. 20° C.	Organic Carbon / Total Nitrogen	Organic Carbon / B. O. D.	Total Nitrogen / B. O. D.
	Total	Organic	Free CO_2 plus carbonate					
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			
Raw	946.8 952.3[a]	906.5[a] 912.0	40.3	182	1410	5.0	0.64	0.129
Settled	702.1 660.0[a]	654.1[a] 612.0	48.0	167	1020	3.8	0.62	0.168
Raw	1035.1 1076.6[a]	1000.3[a] 1044.8	34.8	247	1760	4.1	0.58	0.140
Settled	672.0 701.6[a]	584.8[a] 614.4	87.2	128	1410	4.6	0.42	0.091
Raw	768.0 808.5[a]	713.1[a] 753.6	54.9	187	1360	3.9	0.54	0.137
Settled	628.1 648.5[a]	573.6[a] 594.0	54.5	172	850	3.4	0.68	0.202
Raw	1400.0 1300.0[a]	1303.0[a] 1203.0	97.0	339	2000	3.4	0.63	0.169
Settled	941.0 928.6[a]	941.0[a] 928.6	0.0	259	1680	3.6	0.56	0.154
Raw	790.6 807.8[a]	709.1[a] 726.2	81.6	182	1090	3.9	0.66	0.167
Settled	704.4 723.3[a]	667.7[a] 686.6	36.7	170	1120	3.9	0.60	0.152
Av.	859.8	806.4	53.5	203.3	1370	3.96	0.59	0.151

[a] Calculated.

Table V—Stockyards Wastes

Sample	Carbon			Total Nitrogen	5-Day B. O. D. 20° C.	Organic Carbon / Total Nitrogen	Organic Carbon / B. O. D.	Total Nitrogen / B. O. D.
	Total	Organic	Free CO_2 plus carbonate					
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			
1	372.0 467.0[a]	279.6[a] 374.6[a]	92.4	51.2	620	6.4	0.52	0.083
2	188.9 183.6[a]	140.9[a] 135.6	48.0	16.0	262	8.6	0.53	0.061
3	413.3 411.4[a]	334.3[a] 332.0	79.0	51.2	590	6.5	0.56	0.087
4	248.4 253.2[a]	183.6[a] 188.4	64.8	24.8	295	7.5	0.63	0.084
5	207.6 191.0[a]	155.4[a] 139.4	51.6	25.6	237	5.7	0.62	0.108
6	484.2 497.3[a]	428.5[a] 441.6	55.7	56.0	580	7.7	0.77	0.097
7	139.2 144.0[a]	91.2[a] 96.0	48.0	16.0	135	5.9	0.69	0.119
8	528.0 525.6[a]	470.4[a] 468.0	57.6	67.2	607	6.9	0.77	0.111
Av.	328.4	266.2	62.2	38.5	416	6.9	0.64	0.094

[a] Calculated.

one is as determined. Total carbon in this sewage is made up of about 50 per cent carbon dioxide, which is due partly to carbonates. This carbon undoubtedly has no oxygen demand. There was no appreciable amount of nitrate-nitrite nitrogen.

The results of analyses of activated sludge effluents from the North Side Treatment Works are shown in Table III. It is interesting to note that the organic carbon is low as compared with the carbon dioxide and that the nitrogen is much lower in proportion to the carbon than in the raw sewage. The 5-day oxygen demand is also lower in proportion to the carbon than in the raw sewage.

Industrial Wastes—Results of analyses of tannery wastes are shown in Table IV. These wastes were obtained from an experimental treatment plant at the J. Greenebaum Tanning Company, a chrome tan factory. The values for carbon, nitrogen, and oxygen demand show the waste to be much stronger than raw sewage. The proportion of carbon to nitrogen, however, is about the same as for sewage.

The analyses of stockyards wastes, shown in Table V, are from 12-hour composite samples collected in sewers near the yards. The strength of the waste varies considerably depending upon the time and place of sampling. The ratio of nitrogen to carbon is lower than in sewage or tannery waste.

Refinery wash water from the Corn Products Refining Company (Table VI) contains very little nitrogen although the oxygen demand and carbon are high. The waste, collected hot, contains little or no carbon dioxide.

Relation of Organic Carbon to Other Determinations

Table VII shows the averages of carbon-nitrogen, carbon-B. O. D., and nitrogen-B. O. D. ratios for corn products, stockyards, raw sewage, and tannery wastes. Although the carbon-nitrogen ratios vary from 3.96 to 42.7, the carbon-oxygen demand ratios are quite constant, varying only from 0.55 to 0.65, a maximum difference of 10 per cent from the mean of 0.61. This constant value indicates a relationship between the organic carbon content and the 5-day oxygen demand, supporting the theory that the first stage of the oxygen-demand curve is a carbon oxidation. The activated

Table VI—Wastes from Corn Products Refining Company

Sample	Carbon			Total Nitrogen	5-Day B. O. D. 20° C.	Organic Carbon / Total Nitrogen	Organic Carbon / B. O. D.	Total Nitrogen / B. O. D.
	Total	Organic	Free CO_2 plus carbonate					
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			
1	310.2 301.4	310.2 301.4	0.0	3.7	480	82.0	0.63	0.008
2	340.4 319.2	340.4 319.2	0.0	10.4	445	31.7	0.70	0.023
3	310.3 302.4	310.3 302.4	0.0	9.6	475	31.9	0.65	0.020
4	346.8 346.3	346.8 346.3	0.0	10.4	510	33.3	0.60	0.020
5	430.3 420.5	430.3 420.5	0.0	10.4	560	40.9	0.70	0.008
6	383.3 406.2	383.3 406.2	0.0	14.0	620	28.1	0.63	0.023
7	541.2 546.5	541.2 546.5	0.0	12.0	775	45.3	0.70	0.016
8	583.8 572.4	583.8 572.4	0.0	12.0	980	48.1	0.60	0.012
Av.	403.8	403.8	0.0	10.3	606	42.7	0.65	0.016

sludge effluent with a carbon-nitrogen ratio of 11.8 and a carbon-B. O. D. ratio of 4.1 is in a different stage of oxidation and cannot be compared directly with the raw sewage or trade wastes.

Table VII—Comparison of Carbon-Nitrogen, Carbon-B. O. D., and Nitrogen-B. O. D. Ratios

	Waste from Corn Products Refining Co.	Waste from Stockyards	Raw Sewage North Side Treatment Works	Wastes from J. Greenebaum Tanning Co.	Average
Ratio organic carbon to nitrogen	42.7	6.9	4.0	3.96	14.4
Ratio organic carbon to B. O. D.	0.65	0.64	0.55	0.59	0.61
Diff. from average, %	6.6	5.0	10.0	3.2	6.1
Ratio nitrogen to B. O. D.	0.016	0.094	0.143	0.151	0.101
Diff. from average, %	84.0	6.9	41.5	49.5	45.5

As we would expect, we find no correlation between the values found for the nitrogen–oxygen demand ratios from the sewage and trade wastes. These ratios vary from 0.016 to 0.151. The nitrogen-oxygen demand ratios for the different wastes seem to be similar only when the carbon-nitrogen ratios are similar. For instance, the nitrogen-B. O. D. ratio for tannery waste is 0.151 and for raw sewage 0.143, whereas the carbon-nitrogen ratios are 3.96 and 4.0, respectively. The carbon–oxygen demand ratios are 0.59 and 0.55. When we compare corn products waste and raw sewage with carbon-nitrogen ratios of 42.7 and 3.96, we find the nitrogen–oxygen demand ratios of 0.016 and 0.143, whereas the carbon–oxygen demand ratios are 0.65 and 0.55. The total carbon–oxygen demand ratios are not constant because of the variation in the free and combined carbon dioxide.

Literature Cited

(1) Bauer, O., and Deiss, E., "Sampling and Analysis of Iron and Steel," p. 131, McGraw-Hill, 1915.
(2) Friedemann, T. E., and Kendall, A. I., *J. Biol. Chem.*, **82**, 45 (1929).
(3) Schollenberger, C. J., J. Ind. Eng. Chem., **8**, 1126 (1916).
(4) White, J. W., and Holben, F. J., *Ibid.*, **17**, 83 (1925).

Effect of Light on Determination of Ethylene[1]

J. Louis Oberseider and J. H. Boyd, Jr.

The Atlantic Refining Company, 3144 Passyunk Ave., Philadelphia, Pa.

In the course of the determination of ethylene in gaseous mixtures of paraffin and olefin hydrocarbons, separated at atmospheric pressure from cracked oils, inaccuracies may occur in the analysis because absorption in bromine water continues slowly after many passes if the apparatus is exposed to direct daylight or artificial light. To the knowledge of the authors, there is no mention of this phenomenon in standard texts (*1*, *2*, *3*, *4*) on gas analysis.

The analyses were made in a modified Bureau of Mines Orsat apparatus. Acid gases and unsaturates, with the exception of ethylene, were absorbed in a 30 per cent caustic potash solution and an 87 per cent sulfuric acid, respectively. Ethylene was then determined by bubbling the gas three times through a Williams pipet containing a 33 per cent saturated solution of bromine water at an approximate rate of 15 cc. per minute, and subsequently through caustic potash solution to remove the bromine vapors. This should remove the ethylene from most gases, and repeating the operation should remove no more gas. With direct daylight shining on the apparatus, however, absorption continued even after making fifteen passes.

By painting the Williams pipet black except for a narrow vertical strip, and shielding the buret from direct light, complete absorption was obtained after three or four passes.

The cause of the continuous absorption in the presence of direct light is believed due to the well-known reaction between bromine and the heavier paraffin hydrocarbons. Some evidence in the support of this was obtained by passing a sample of *n*-butane through the bromine solution in the presence of direct light. Absorption was still taking place after ten passes. Using the shielded pipet no absorption took place.

[1] Received November 29, 1930.

Literature Cited

(1) Dennis, L. M., "Gas Analysis," MacMillan, 1920.
(2) "Gas Chemist's Handbook," American Gas Assocn., 1922.
(3) Parr, S. W., "The Analysis of Fuel, Gas, Water and Lubricants," McGraw-Hill, 1922.
(4) White, A. H., "Technical Gas and Fuel Analysis," McGraw-Hill, 1920.

Measurement of Turbidity with a Spectrophotometer[1,2]

With Especial Reference to Sugarhouse Products

R. T. Balch

Bureau of Chemistry and Soils, Washington, D. C.

As it is frequently desirable to measure the turbidity of sugar liquors during the course of sugar manufacture or refining, a number of methods have previously been proposed. Adoption of these methods has not, however, been extensive because, it is believed, too large errors are introduced owing to lack of color compensation. In the method described, transmission of light at a definite wave length is taken as a measure of turbidity, and color is compensated by using as a standard a portion of the same sugar solution from which suspended solids are removed. For the preparation of this standard, filtration through paper with the aid of a slow-filtering grade of commercial kieselguhr is recommended in place of asbestos or sand. Turbidities are expressed in $-\log t$ values as being the most convenient method, in spite of the fact that $-\log T$ values are not strictly proportional to the concentration or the depth of the suspension.

FROM the early days of the sugar industry it has been known that suspended solids in sugar juices and sirups have detrimental effect upon the quality of the sugar produced therefrom. In raw sugar manufacture it has a bearing on the cleanliness and filterability of the sugars, and in the manufacture of direct consumption and refined sugars suspended material may be responsible for the production of off-colored or dull-appearing sugars.

It is therefore frequently desirable to introduce a turbidity control of various clarification processes, but owing to the lack of adequate methods or standards, such a control has not been widely adopted. The principal objection to the methods recommended for use in sugar technology (*4, 5, 8*) is that usually no provision is made, or it is inadequately made, to compensate for the color of the product, which may introduce considerable error. Some of the methods for determining turbidity require, too, the use of turbidity standards which are frequently unstable and cannot, therefore, be highly recommended. The ideal method is one which will permit the determination of turbidity in either colored or colorless solutions with equal accuracy, and in which the results may be expressed in numerical values with or, preferably, without reference to synthetic turbidity standards. The method which is to be described is believed to approach this ideal more closely than any yet proposed.

Theory and Brief Description of Methods Used for Determining Turbidity

When a turbid solution is illuminated by a beam of light, a portion of the incident light is reflected, a portion is absorbed by the suspended particles and by the solution, particularly if colored, and a portion of the light is transmitted through the solution. One group of methods measures the intensity of the scattered light or the Tyndall beam in relation to the incident or standard light. Another group determines the masking effect or absorption of light by the particles (and color), the so-called extinction methods, or, inversely, the intensity or the percentage of the incident light that is transmitted. There are so many factors such as the number, size, shape, and other physical characteristics, of the particles which affect the intensity of either the Tyndall or the transmitted light, that the mathematical expressions which have been developed (*11*) relating some of these factors cannot be applied except under rather ideal conditions. In nephelometric analysis (*12*), for instance, it is possible to control conditions sufficiently to obtain a considerable degree of precision, but such is not the case when attempting to determine the quantity of suspended material in a sugar liquor from a measure of its turbidity. The most disturbing factors are the varying composition and the varying size of particles, which covers the entire range from coarse to molecular dispersion.

This is, perhaps, not as serious as it appears since in practice the comparative turbidities and not the actual quantity of material present is the chief concern. It does not matter greatly whether the particles are relatively large or small, heavy or light in density, except to suggest means for their removal. It is desirable, however, to have a method which gives comparable values—that is, one which gives with sufficient accuracy the relative turbidities of sirups or juices of the same general type.

As already indicated, one of the principal difficulties with existing methods is the lack of color compensation. Since so many shades and intensities of color are encountered, it is not very practicable to attempt the preparation and use of synthetically colored solutions or glass screens. In the method which the writer proposes, color compensation is accomplished by using a portion of the sugar solution to be tested from which material responsible for visible turbidity has been removed. This immediately brings up the question whether it is possible to remove suspended material without altering the color and, if so, the best method by which this may be accomplished.

In accurate colorimetric work, particularly in spectrophotometric analysis, it is required that all material causing turbidity be removed from the solution before making the color determination. For this purpose, various methods have been proposed. Peters and Phelps (*7*) recommend filtration through specially prepared asbestos, whereas Lunden (*6*) claims that ultracentrifuging or filtration through sand are the only proper methods, and Spengler and Landt (*10*) that special filters of other types are required. Honig and Bogstra (*3*) also recommend sand filtration but apparently adopt filtration through kieselguhr in spite of the fact that various investigators claim that this agent has a selective adsorption action on color.

It is very doubtful whether it is actually possible to remove all the material causing turbidity, if judged by the Tyndall beam, without changing the color of the solution. It is well known that small particles within the range of colloid dimensions (5 to 200 mμ) and even those which exceed this

[1] Received December 10, 1930. Presented before the Division of Sugar Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Contribution No. 100, Carbohydrate Division, Bureau of Chemistry and Soils.

size to some extent exhibit color phenomena by both reflected and transmitted light. Thus, if the clarification process is sufficiently efficient to remove suspended particles within this range of size, the apparent color of the solution would, without question, be changed to some extent. This fact accounts, it is believed, for the diversity of opinions as to the best method for clarifying sugar solutions for colorimetric analysis and the belief of some investigators that kieselguhr selectively adsorbs color. It is the author's opinion that this agent removes only by mechanical means, and not by true adsorption, particles within the range of size which affects color to a slight extent. These particles are not completely removed by either asbestos or sand under the procedures generally recommended for preparing sugar solutions for spectrophotometric analysis.

The results of some preliminary experiments conducted by the author substantiate this view. For example, a raw sugar solution, clarified with kieselguhr, had the same $-\log t$ value regardless of whether 1, 2, or 3 per cent of filter aid (based on sugar solids) was used or whether the solution was filtered immediately or after it had stood for some time. From our knowledge of adsorption, considered in its broader sense, one would expect differences in the color of the solution treated in these different ways unless it were assumed that maximum adsorption occurred with the smallest quantity filter aid used and in the minimum time period, which are very doubtful assumptions to make. Kieselguhr unquestionably removes particles of smaller size than is possible by filtration through asbestos or sand. However, the minimum size of particles which are removed by these various agents has never been determined. The experiments conducted by the writer indicate that true adsorption of color is lacking or extremely slight at the most, so that it is permissible to use kieselguhr for the preparation of sugar solutions for either colorimetric analysis or as a standard in compensating for color in turbidity measurements.

Description of Spectrophotometric Method for Measuring Turbidity

The method proposed for measuring turbidity is based upon the principle of measuring the transmission of light through the turbid solution, using as a standard to compensate for color a portion of the same sugar solution from which material causing turbidity has been removed. The principles involved and the apparatus used are the same as for spectrophotometric color analysis (*7*, *9*).

Lambert and Beer's law, which is used so extensively in spectrophotometric analysis, correlating transmission of light and concentration of color and thickness of solution, unfortunately does not hold exactly for turbid solutions. Until it is possible to develop more adequate relationships it is proposed to assume the validity of Lambert and Beer's law and to express turbidities as $-\log t$ values in accordance with the following equation:

$$-\log t = \frac{1}{cb}(-\log T)$$

where t = transmittancy reduced to unit conditions as regards concentration and thickness of solution, c = concentration of the solution expressed as grams of dry substance per 1 cc.; b = thickness of solution expressed in cm.; and T = the transmitted fraction of the incident light.

In order to determine how closely this relationship might be expected to hold in the case of suspensions, a series of bentonite suspensions were prepared whose concentrations were made to range from 0.25 to 2.00 grams per 100 cc. (coarse particles included) by aliquoting from a 5 per cent suspension. The $-\log t$ values of these suspensions were then determined at 560 mμ in cells of different length with a Keuffel and Esser color analyzer. Between the high and the low concentrations, a maximum variation of 15 per cent in the $-\log t$ value was observed, whereas with different length tubes the maximum variation in $-\log t$ values was about 10 per cent. These variations are probably somewhat exaggerated by the inability to obtain a correct aliquot of the stock suspension owing to the rapid settling of the larger particles. In spite of these divergences from Lambert and Beer's law, it is considered advisable to express turbidities as $-\log t$ values, as this affords a fairly close index of relative turbidities with sugar liquors of most types and undoubtedly better than by any other method so far proposed.

In order to ascertain whether the method of color compensation is satisfactory and whether turbidities can be measured in colored solutions as accurately as in colorless solutions, two series of bentonite suspensions in sugar sirups were prepared. One sirup was colorless and the other was colored strongly with caramel to simulate a sirup prepared from a dark raw sugar. The concentration of bentonite in each series ranged from 0.25 to 2.00 grams per 100 cc. of final solution. The transmission of light was measured at 560 mμ through a 1-cm. cell, again with a Keuffel and Esser color analyzer. The standards for the two solutions were, of course, a portion of the colorless sirup for the one series of determinations, and a portion of the colored sirup for the other series. The data given in Table I show conclusively, it is believed, that when color is properly compensated, the transmission of light gives a very satisfactory measure of turbidity regardless of the color of the solution.

Table I—Transmission of Light through Bentonite Suspensions
(At 560 mμ in 1-cm. cell)

Bentonite Concentration	Transmission through Bentonite	
	Colorless sirup	Colored sirup[a]
Grams/100 cc.	%	%
0.00	100.0	100.0
0.25	84.3	84.5
0.50	70.5	70.8
0.75	58.3	58.4
1.00	48.7	49.1
1.50	33.1	33.6
2.00	22.9	22.6

[a] Colored with caramel.

Preparation of Samples for Turbidity Determination

It is well known that dilution of many impure sugar solutions causes an increase in turbidity; hence it is important that the procedure for preparing the solutions for turbidity measurements be carefully standardized. Juices and factory sirups can, as a rule, be filtered with kieselguhr without dilution, a procedure which is recommended by all means. Difficulties exist, however, when dealing with solid and semi-solid products, and undoubtedly differences of opinion will arise as to the selection of the density to which dilutions should be made. Since it is necessary to filter a portion of the sugar solution, it will probably not be practicable to exceed 60 per cent solids to any material extent except for a very few high-purity products; but for comparative purposes it is believed to be permissible to prepare a more dilute solution such as one of a 50 per cent solids concentration. Such details will have to be worked out by the person making the tests, keeping in mind, however, that whatever concentration is decided upon, all similar products must be diluted to the same concentration if comparative values are to be obtained. This is a rather unsatisfactory procedure to recommend, but it cannot very well be avoided.

Clarification of that portion of the sample to be used for color compensation is accomplished by filtration with the aid of kieselguhr. Since it is desired to remove as much of the suspended matter causing turbidity as is possible, the

slower filtering grades of kieselguhr[3] are more satisfactory than the faster ones. The latter grades very frequently yield filtrates which are not entirely free even from visible turbidity. Even the best quality filtrates usually show a distinct Tyndall beam when an intense source of light is used and the observation is made in a dark room, so that this criterion cannot be used and it seems necessary to adopt a purely arbitrary method of filtration. The method to be described will, in the writer's opinion, give very satisfactory results with practically all sugarhouse products with the possible exception of those of low purity or those which have undergone partial fermentation. The measurement of turbidity of these products will probably never be desired, and therefore need not be considered.

A 100- to 200-gram portion of the sugar solution to be tested is filtered with 2 to 10 per cent of kieselguhr (based on sugar solids). The quantity of filter aid to be used depends upon the quantity and character of the suspended material affecting filtration. The more resistant to filtration this material is, the greater the quantity of kieselguhr required. In general, the minimum quantity stated will be sufficient to filter high-purity products satisfactorily but, for cane juice or lime-defecated juices and sirups, the maximum will undoubtedly be necessary. After mixing the kieselguhr very thoroughly with the sample, it is filtered at room temperature under diminished pressure through paper in a Büchner funnel which is attached to a fractional distillation receiver. The source of vacuum may conveniently be a water-jet pump. After 25 to 50 grams of the solution have filtered, the remainder is received in another container, the change of containers being made without disturbing the vacuum. This last portion should appear brilliantly clear by transmitted light of ordinary intensity. For more precise determinations of the $-\log t$ values, it will be desirable to obtain as accurately as possible the solids content of this filtered sirup, but for most purposes, the per cent solids by refractometer will suffice.

Measurement of Turbidity

The clarified portion of the sugar solution is placed in one cell of the spectrophotometer as a standard, and in the other cell is placed the turbid portion freed from coarsely suspended material by straining through approximately 200-mesh bolting silk and freed from air bubbles by subjecting the sample to vacuum, conveniently in the fractional distillation receiver at the time the filtration is being made. The length of cell to be used depends upon the color and turbidity of the sample. With the type of instrument used by the writer, 10-cm. cells were used for the 50 per cent solutions of granulated sugars, whereas for products as dark and turbid as raw sugar solutions of the same concentration, 1-cm. cells were used. The transmission measurement may be made at any convenient wave length, such as at 560 mμ. As in all optical measurements which depend upon personal observation, the accepted reading is the average of a number of settings of the instrument.

It was interesting to note that the per cent transmission of light through turbid sugar solutions, and to a lesser degree through bentonite suspensions, varied with the wave length of light, greater transmission occurring in the red end of the spectrum and less in the violet end. This probably indicates the presence of particles of such a size as to contribute to the color of the solution, a portion of them being removed by kieselguhr. The difference in percentage of light transmitted at certain definite wave lengths at each end of the spectrum might conceivably be an approximate measure of the average or typical size of particles present in the sugar solution which are removable by kieselguhr and which contribute to the color. To determine this point definitely, however, would require a painstaking study of the size of particles and of the relationship between the size of the particles and the color of the solution, which is beyond the scope of this paper.

As previously indicated, it seems preferable to calculate the readings to $-\log t$ values in order to have a common basis for comparing sugar products of different types. If the instrument is calibrated to read directly in $-\log T$ units, this value is simply divided by the product of the concentration of the solution (grams solids per cc.) and length of cell (cm.) to obtain $-\log t$; on the other hand, if the instrument gives the percentage of light transmitted or T, $-\log T$ is first calculated from the equation

$$-\log T = \log \frac{1}{T}$$

which value, when treated as above, gives $-\log t$.

Results on Sugars

A number of granulated and raw sugars were examined by the spectrophotometric method for determining turbidity, and the results are given in Table II.

Table II—Turbidities ($-\log t$) of Granulated and Raw Sugars

Sugar	c	b	T	$-\log T$	$-\log t$
	Gram/cc	*Cm.*			
Granulated					
1	0.615	10	0.650	0.18709	0.030
2	0.615	10	0.505	0.29671	0.048
3	0.615	10	0.685	0.16431	0.027
4	0.615	10	0.425	0.37161	0.059
5	0.615	10	0.320	0.49485	0.081
6	0.615	10	0.600	0.22185	0.036
7	0.615	10	0.620	0.20761	0.034
8	0.615	10	0.325	0.48812	0.079
9	0.615	10	0.690	0.16115	0.026
Cube					
10	0.615	10	0.880	0.05552	0.009
Raw cane					
1[a]	0.615	1	0.235	0.62893	1.023
2[a]	0.615	1	0.340	0.46852	0.762
3[a]	0.615	1	0.120	0.92082	1.497
4[a]	0.615	1	0.005	2.30103	3.742
5[b]	0.615	1	0.360	0.44370	0.722
6[c]	0.615	1	0.380	0.42022	0.683
7[c]	0.615	1	0.400	0.39794	0.647
8[c]	0.615	1	0.295	0.53018	0.862
9[c]	0.615	1	0.455	0.34199	0.556

[a] Poor filtering sugars. [b] Fair filtering sugar. [c] Good filtering sugars.

As was to be expected, cube sugar showed distinctly lower turbidity than standard granulated sugars. In the case of raw cane sugars there is a general relationship between turbidity and filtering quality, as determined with the Dawson filter (*2*) but, since the specific physical character of the suspended matter has such a pronounced effect upon filtration (*1*), a high degree of correlation could not be expected.

In Table III is shown a comparison between $-\log t$ values and percentage of suspended material contained in the sugar. The latter values are based on the differences in the weight of alcohol precipitates (50 per cent alcohol concentration) before and after filtration of a 50 per cent solution of the sugar with kieselguhr.

Table III—Turbidity in Relation to Suspended Solids in Raw Sugar

Sample	Suspended Solids on Sugar	$-\log t$ at 560 mμ
	%	
4	0.131	3.742
3	0.084	1.497
1	0.084	1.023
2	0.065	0.762
8	0.042	0.862
6	0.036	0.683
9	0.030	0.556
5	0.027	0.722
7	0.026	0.647

[3] Standard Filter-Cel, a product of the Johns Manville Corp., has proved satisfactory.

The correlation in these instances is about as good as could be expected in view of the variation in the specific character of the material causing turbidity and the errors involved in the data, particularly the percentage of suspended solids.

Conclusions

Although it has not been possible to test the spectrophotometric method for estimating turbidities very extensively, this method appears to have interesting possibilities. It is believed that the principle on which the method is based is satisfactory and that the method affords comparable results with various types of sugarhouse products. From a practical point of view, however, the method has at least one drawback. The instrument used in this study is rather expensive, and as a result only a few sugar laboratories are equipped with one but, since the light transmission needs to be measured only at a single wave length, it is possible that a simplified apparatus would give satisfactory results.

Literature Cited

(1) Balch, Unpublished report.
(2) Dawson, "Testing Apparatus and Method for Determining the Filterability of Raw Sugars," paper presented before the Division of Sugar Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 9, 1925.
(3) Honig and Bogstra, *Facts About Sugar*, **23**, 446, 470, 494 (1928).
(4) Horne and Rice, Ind. Eng. Chem., **16**, 626 (1924).
(5) Ingersoll and Davis, *Ibid.*, Anal. Ed., **2**, 248 (1930).
(6) Lunden, *Z. Ver. deut. Zuckerind.*, **77**, 709 (1927).
(7) Peters and Phelps, Bur. Standards, *Tech. Paper* **338** (1927).
(8) Smith, *Intern. Sugar J.*, **26**, 381 (1925).
(9) Spencer-Meade, Handbook for Cane Sugar Manufacturers and Their Chemists, p. 293, Wiley, 1929.
(10) Spengler and Landt, *Z. Ver. deut. Zuckerind.*, **77**, 431 (1927).
(11) Wells, *Chem. Rev.*, **3**, 331 (1927).
(12) Yoe, "Photometric Chemical Analysis. II—Nephelometry," Wiley, 1929.

Separation of Calcium and Magnesium by Molybdate Method[1]

R. C. Wiley

University of Maryland, College Park, Md.

Calcium molybdate is quite insoluble in a solution that is nearly neutral.

Calcium may be determined accurately by precipitating as the molybdate. The presence of residual ammonium molybdate in the washings from the calcium molybdate does not prevent the precipitation of magnesium as the magnesium ammonium phosphate, and the presence of ammonium salts does not interfere with the determination of calcium as molybdate.

Calcium and magnesium may be determined in much less time when the molybdate method for calcium is used than when the calcium is precipitated by the oxalate method.

Many naturally occurring minerals contain calcium and magnesium. It is customary to separate the calcium from the magnesium by making a double precipitation of the calcium as the oxalate, evaporating the filtrates to a smaller volume and then making a double precipitation of the magnesium. There is no question that this method of determining calcium and magnesium is accurate. However, while it is accurate, it is likewise tedious and time-consuming. The object of the present investigation was to find, if possible, a method whereby the double precipitations could be eliminated, thus saving a considerable amount of time.

Smith and Bradbury (*1*) found that calcium molybdate was only slightly soluble in water. Magnesium molybdate, on the other hand, is quite soluble in water. For these reasons the writer thought it might be possible to separate these two elements by precipitating the calcium as the molybdate, washing the calcium molybdate well, and then precipitating the magnesium from filtrate and washings as magnesium ammonium phosphate in the usual way. It was hoped that the presence of the molybdate in the filtrate would not interfere with the precipitation of magnesium as magnesium ammonium phosphate, as does an oxalate.

Solutions Used

The solutions used, aside from the ordinary laboratory reagents, were as follows:

(1) Carefully standardized solutions of calcium chloride made by weighing out calcite, dissolving it in hydrochloric acid, and evaporating to dryness over a water bath, and then making up to the required volume with distilled water. The calcium in solution was determined by the molybdate method, and also by the permanganate method. The solution was about 0.1 *N*.

(2) A solution of magnesium nitrate made by dissolving magnesium nitrate in distilled water. The magnesium in solutions was determined by precipitating as magnesium ammonium phosphate, and igniting and weighing in the usual way. The solution was about 0.15 *N*.

(3) A solution of ammonium molybdate about 0.4 *N*, slightly acid with acetic acid.

(4) A solution of ammonium molybdate about 0.4 *N* slightly alkaline with ammonium hydroxide.

Plan of Procedure for Precipitation in Alkaline Solution

The calcium chloride solution and the magnesium nitrate solution were carefully pipetted into the same beaker. The solution was heated to boiling, a drop or two of concentrated ammonium hydroxide added, and the molybdate solution added at the rate of about one drop per second until an excess was present. The solution was then boiled until the supernatant liquid was clear, and allowed to stand until cool. The precipitate was filtered from the solution by means of a tared Gooch crucible in which the layer of ordinary asbestos had been reinforced by a little ground asbestos. The suction on the crucible was carefully regulated. The precipitate was carefully washed with ten portions of hot distilled water of about 10 cc. each. The crucibles were then placed in an oven at 130° C. and dried for 30 minutes, then ignited and weighed. The filtrate was used for the determination of magnesium without evaporation. Its volume was about 100 to 125 cc. The magnesium was determined without double precipitation in the usual way; that is, by precipitating as the magnesium

[1] Received August 16, 1930.

ammonium phosphate, filtering in a Gooch, igniting, and weighing as magnesium pyrophosphate. The procedure for precipitation of calcium in an acid solution is the same as for an alkaline solution, except that a slightly acid solution of ammonium molybdate is used and no ammonium hydroxide is added.

Table I gives results found when the molybdate solution used was slightly alkaline. The factor 0.2002 was used to convert calcium molybdate to calcium.

Table I—Effect of Precipitating Calcium as Molybdate in Slightly Alkaline Solution

Magnesium		Calcium Found	
In original soln.	Found after removal of calcium	By permanganate method, original soln.	By molybdate method in presence of magnesium
Gram	*Gram*	*Gram*	*Gram*
0.0449	0.0443	0.510	0.0511
0.0442	0.0445	0.514	0.0514
0.0447	0.0445	0.508	0.0511
0.0446	0.0446	0.516	0.0512
	0.0447		0.0511
	0.0447		0.0514
	0.0445		0.0512
	0.0447		0.0515
	0.0443		0.0519
			0.0512
Av. 0.0446	0.0445	0.512	0.0513

The results of the above experiment show that calcium can be separated from magnesium by the molybdate method. They show that magnesium is not adsorbed, occluded, or coprecipitated along with the calcium molybdate precipitate, and also that the results for magnesium are the same as they would be if no ammonium molybdate had been present when it was precipitated. This is in contrast to the results obtained when magnesium is precipitated in a solution containing the salts of oxalic acid.

Table II—Effect of Precipitating Calcium as Molybdate in Slightly Acid Solution

Magnesium		Calcium Found	
In original soln.	Found after removal of calcium	By permanganate method, original soln.	By molybdate method in presence of magnesium
Gram	*Gram*	*Gram*	*Gram*
0.0446	0.0446	0.0512	0.0515
	0.0447		0.0514
	0.0446		0.0513
	0.0451		0.0515
	0.0446		0.0515
	0.0448		0.0512
	0.0447		0.0516
	0.0448		0.0511
Av. 0.0446	0.0447	0.0512	0.0514

The results given in Table II show that it is possible to separate calcium and magnesium by the molybdate method in a solution slightly acid with acetic acid. The results are almost exactly the same as those obtained when the solution in which the precipitation is made is slightly alkaline with ammonium hydroxide.

The calcium in the solution of calcium chloride was determined by the molybdate method when no magnesium was present. Four determinations were made; 0.0511, 0.0513, 0.0512, and 0.0514 gram of calcium were found by this method.

Since in most cases where calcium and magnesium are to be determined ammonium salts are present in solution, it was decided to determine whether the presence of ammonium chloride would exert any solvent effect upon the calcium molybdate precipitate. Therefore, portions of 25 cc. of the calcium solution were pipetted into each of eight beakers, and 3 grams of ammonium were weighed out on a rough balance and added to each solution. The precipitate was then thrown down in the usual way in a slightly alkaline solution. The results are given in Table III.

From Table III it will be seen that the presence of ammonium salts does not interfere with the precipitation of calcium by the molybdate method.

Table III—Effect of Ammonium Chloride on Calcium Found by Molybdate Method in Slightly Alkaline Solution

Calcium Present	Calcium Found
Gram	*Gram*
0.0512	0.0508
	0.0512
	0.0510
	0.0506
	0.0514
	0.0514
	0.0518
	0.0506
Av. 0.0512	0.0511

Table IV shows results obtained with varying amounts of calcium and magnesium in a slightly alkaline solution in the presence of 3 to 5 grams of ammonium chloride.

Table IV—Effect of Separation of Varying Quantities of Calcium and Magnesium

Calcium			Magnesium		
Present	Found	Difference	Present	Found	Difference
Gram	*Gram*	*Gram*	*Gram*	*Gram*	*Gram*
0.0500	0.0502	+0.0002	0.0125	0.0127	+0.0002
0.0500	0.0504	+0.0004	0.0125	0.0123	−0.0002
0.0500	0.0500	0.0000	0.0125	0.0123	−0.0002
0.0500	0.0501	+0.0001	0.0125	0.0123	−0.0002
0.0500	0.0500	0.0000	0.0129	0.0127	−0.0002
0.0500	0.0498	−0.0002	0.0129	0.0129	0.0000
0.0500	0.0502	+0.0002	0.0129	0.0127	−0.0002
0.0500	0.0500	0.0000	0.0129	0.0128	0.0001
0.0500	0.0496	−0.0004	0.0129	0.0123	−0.0006
0.0500	0.0500	0.0000	0.0129	0.0129	0.0000
0.0200	0.0202	+0.0002	0.0316	0.0314	−0.0002
0.0200	0.0199	−0.0001	0.0316	0.0318	+0.0002
0.0200	0.0200	0.0000	0.0316	0.0316	0.0000
0.0200	0.0205	+0.0005	0.0316	0.0316	0.0000
0.0200	0.0202	+0.0002	0.0316	0.0316	0.0000
0.0200	0.0197	−0.0003	0.0316	0.0316	0.0000
0.0200	0.0200	0.0000	0.0316	0.0316	0.0000
0.0200	0.0200	0.0000	0.0316	0.0314	−0.0002
0.0200	0.0201	+0.0001	0.0732	0.0730	−0.0002
0.0200	0.0201	+0.0001	0.0732	0.0733	+0.0001

These results show a clean separation of calcium and magnesium.

Comment and Discussion

The precipitate formed by ammonium molybdate and a soluble calcium salt is a white crystalline solid. The crystals are quite hard and dense and settle quickly. It is easily filtered and washed. When precipitating this compound, a stirring rod should not be placed in the beaker for, if the beaker is scratched, crystals form at the point scratched and these crystals are very difficult to remove with a policeman.

The precipitate may not appear immediately. The calcium ion and the molybdate ion may both be present in 0.01 N to 0.05 N concentration for a few minutes without precipitation. The white precipitate which makes its appearance after a few minutes is rather soluble when first formed. After boiling for 10 to 15 minutes, however, it becomes highly insoluble. Sometimes the precipitate is not pure calcium molybdate but upon ignition in a Gooch it is converted into calcium molybdate. The color of the calcium molybdate should be pure white, as a blue color upon ignition shows reduction. It may be ignited to constant weight in about 10 to 15 minutes in a Gooch. The white precipitate must not be ignited in a filter paper because it will be reduced.

Water saturated with the white precipitate is less than 0.00005 N with respect to the molybdate ion. Its solubility does not increase upon ignition nor is it hygroscopic. A Gooch crucible may be used over and over again in the filtration.

The crystals of this compound start to form within a minute or two after the addition of the ammonium molybdate solution. If the molybdate solution is added too rapidly, the crystals tend to stick to the sides of the beaker. They may be then removed with a horn spatula or quickly detached by rubbing a few fine crystals of ammonium chloride against them with a policeman. It has been found that it need not be more than 45 minutes from the time the molybdate is added to the solution until the crystals have grown to sufficient size to be readily filtered.

It is believed that this method should prove useful in the analysis of limestones and dolomites, for it is shown that the results obtained without any double precipitations or evaporation are as exact as could be obtained by making a double precipitation of the calcium by the oxalate method and then evaporating down the filtrates and washings and making a double precipitation of the magnesium by the usual method. The method herein described thus eliminates two precipitations and an evaporation without any sacrifice of the accuracy of the determinations and at a considerable saving of time.

Like other molybdates this precipitate is quite soluble in concentrated mineral acids and in strong bases. Therefore, care should be taken that the solution from which it is precipitated be nearly neutral.

The writer prefers to precipitate calcium from a slightly alkaline solution. No trace of molybdenum was found in the magnesium precipitates.

Reducing gases should not be allowed to come in contact with the calcium molybdate during ignition.

A large excess of ammonium molybdate should be avoided. Before filtering, a drop of the supernatant liquid should be tested with a saturated solution of pyrogallol in chloroform. A brown coloration denotes an excess of molybdate. This test is not decisive unless the solution tested has been boiled at least 10 minutes, for the precipitate of calcium molybdate forms rather slowly.

Literature Cited

(1) Smith and Bradbury, *Ber.*, **24**, 2930 (1891).

Conductometric Titration of Sulfate and Barium[1]

I. M. Kolthoff and Tohru Kameda

School of Chemistry, University of Minnesota, Minneapolis, Minn.

In the conductometric titration of alkali sulfate with barium chloride, the knick point is found before the equivalence point. The error depends upon the dilution, alcohol content, acidity, and the kind of cations present. Especially in the titration of 0.1 *N* solutions are the results more or less irregular, the deviations being smaller in the titration of lithium sulfate than of potassium sulfate.

In more dilute solutions, the results are reproducible within 1 per cent. Therefore, in series of determinations of sulfate, the application of the conductometric method can be very useful if the standardization is made under the same conditions as the experiments with the unknown.

The deviation from the theoretical results cannot be attributed to a coprecipitation of sulfate. By special experiments it has been shown that the conductivity in the presence of the precipitate is distinctly higher than in the filtrates. This may be caused by the charge of the barium sulfate in suspension and by its influence upon the cell constant.

In the reverse titration of barium with sulfate, the knick point is found nearer the equivalence point though a small deviation of the order of 1 per cent is observed. The conductometric method is very useful in the titration of very dilute solutions in the presence of 30 per cent alcohol.

The mobility of the barium ions is decreased much more by alcohol than that of the alkali or sulfate or chloride ions.

At present, we have neither an inside nor an outside indicator available for the detection of the end point in the direct or reverse titration of sulfate with a barium solution. A potentiometric method cannot be used either, for the reason that there is no suitable indicator electrode for this reaction. Therefore, the application of the conductometric method to the titration of sulfate with barium or the reverse procedure has special advantages. It was first recommended by Dutoit (*1*) in 1910. Though there is an extensive literature on this titration method, there is no general agreement as to its accuracy. According to several authors, the knick point in the sulfate titration occurs before the equivalence point and the results are correspondingly low; a few claim to find accurate results.

From the recent monograph of Jander and Pfundt (*2*), one gets the impression that the conductometric sulfate titration under different conditions gives theoretical results. However, the experimental evidence they present is too poor to make the statement convincing.

In one of the writers' investigations, it was necessary to make a series of analyses of the sulfate content in dilute zinc sulfate solutions, and for this purpose the conductometric method was applied. However, in testing it with solutions of known content, very disappointing results were found, the latter sometimes being more than 5 per cent low. Therefore it was thought necessary to make a more systematic investigation on the reliability of the conductometric titration of sulfate with barium and the reverse procedure. The first part of the work has been carried out in the usual way—i. e., at room temperature, without taking precautions to keep the temperature completely constant. In order to be certain that the unfavorable results could not be attributed to irregular changes in temperature, all the work was repeated by performing the titrations in a thermostat at a temperature of 25° ± 0.05° C. Only this part of the work will be reported.

Apparatus and Solutions Used

Conductivity cells with vertical electrodes were used. They were sealed to a heavy platinum wire, the latter making contact between the electrode and the mercury in the vertical glass tubes fused to the glass of the cell. Thick copper wires dipping in the mercury made the electrical contact in the circuit of the Wheatstone bridge. The biggest part of the conductivity cell dipped into the thermostat during the titration. The microburet with the reagent was mounted above the opening in the upper middle part of the cell. After each addition of reagent, the content of the vessel was mixed by careful shaking, and the final readings were made when the conductivity did not change further after longer standing. In order to prevent a change in concentration by evaporation during the titration, the opening of the cell was closed by a rubber stopper after each addition of reagent.

All the salts used were pure substances. The potassium,

[1] Received October 20, 1930. Chapter from a thesis submitted by Tohru Kameda to the Graduate School of the University of Minnesota, in partial fulfilment of the requirements for the degree of doctor of philosophy.

sodium, and lithium sulfate were chemically pure commercial products, twice recrystallized from water, and dried in the proper way. Normal and tenth-normal solutions were prepared in conductivity water and the strength was controlled by a gravimetric standardization according to reliable procedures. Solutions of purified barium chloride were standardized in a similar way. In part of our titrations, barium acetate was used as a precipitating reagent. Though the acetate ion has a much smaller conductivity than the chloride ion, we cannot recommend this salt for general use. Difficulties are encountered when the solutions contain some kind of an acid. The acetate ions of the reagent form an acetate–acetic acid buffer with the acid in the solution, and the conductivity changes in an irregular way on account of the variation of the hydrogen-ion concentration during the titration. The water used in all the experiments was conductivity water; the acetic acid was purified by distillation over chromic acid and the alcohol over lime.

Titration of Sulfate with Barium Chloride

In the following table, the results of the titrations are reported in a condensed form. In order to save space the changes of the conductivity during the titration and the plotted values for finding the knick point are omitted. In the column expressing the deviation between location of equivalence and knick point, the minus sign means that the knick point occurs before the equivalence point; therefore, too little sulfate is found. In cases where alcohol was added, the titrations were not begun before the temperatures of the solutions were the same as that of the thermostat (25° C.).

In the titrations of lithium sulfate, three sets of readings have been made; one after three to five minutes after addition of the reagent, one after fifteen to thirty minutes' standing, and the last repeated after shaking the cell, the precipitate thus being suspended in the solution.

In most cases the knick point is found before the equivalence point, the error being the largest in the titration of potassium sulfate (deviation about 5 per cent). The addition of a little alcohol (10 per cent) with or without 1 per cent acetic acid has practically no influence upon the results. It should be remarked, however, that the shape of the precipitation curve improves markedly by the addition of alcohol. In titrating 0.1 N potassium sulfate solution in water the conductivity changes during the precipitation more or less in an irregular way, and, therefore, the slope of the line which combines the different points is more or less uncertain. For this reason the titration figures found are not well reproducible. The same holds, though to a lesser extent, in the titration of 0.1 N sodium and lithium sulfate. The titration of 0.1 N sodium sulfate yields better results than that of potassium sulfate, the error being about 2 per cent. Addition of 10 per cent alcohol had no influence; in the presence of 50 per cent alcohol, however, the results are about 6 per cent low. Acetic acid in a concentration of about 1 per cent increases the error from about 2 to 3 per cent, and the combination of 10 per cent alcohol and 1 per cent acetic acid even to 5 per cent. The best results are obtained in the titration of 0.1 N lithium sulfate. Even in the presence of 10 per cent alcohol and 1 per cent acetic acid, the deviation is not larger than about 1 per cent from the theoretical value. In the titration of 0.05 N zinc sulfate the knick point is found about 6 per cent before the equivalence point. It is peculiar that the addition of alcohol improves the results, the error being 5 per cent in the presence of 10 per cent alcohol, 3.5 per cent of 20 per cent alcohol, 2 per cent of 30 per cent alcohol, 0.0 per cent of 40 per cent alcohol, and +1.9 per cent of 50 per cent alcohol. The combination of alcohol and 1 per cent acetic acid has a tendency to make all the results more uniform.

Table I—Titration of Sulfates with Barium Chloride

Sulfate Concn. N	Amount Taken *Millimols*	Sulfate Found *Millimols*	Deviation %	Solvent
		POTASSIUM SULFATE		
0.1	2.498	2.385	−4.5	Water
0.1	2.498	2.378	−4.8	10% alcohol
0.1	2.498	2.378	−4.8	10% alcohol + 1% acetic acid
0.01	0.2463	0.2377	−3.5	Water
0.01	0.2463	0.2399	−2.6	10% alcohol
0.01	0.2463	0.2387	−3.1	30% alcohol
0.01	0.2463	0.2351	−4.5	50% alcohol
0.01	0.2463	0.2387	−3.1	1% acetic acid
0.01	0.2463	0.2327	−5.5	10% alcohol + 1% acetic acid
0.01	0.2463	0.2337	−5.1	10% alcohol + 1% acetic acid
0.01	0.2463	0.2322	−5.7	30% alcohol + 1% acetic acid
0.01	0.2463	0.2237	−9.2	50% alcohol + 1% acetic acid
		SODIUM SULFATE		
0.1	2.420	2.373	−2.0	Water
0.1	2.420	2.383	−1.6	10% alcohol
0.1	2.420	2.273	−6.1	50% alcohol
0.1	2.420	2.348	−3.0	1% acetic acid
0.1	2.420	2.298	−5.1	10% alcohol + 1% acetic acid
0.01	0.2420	0.2374	−1.9	Water
0.01	0.2420	0.2369	−2.1	Water
0.01	0.2420	0.2349	−2.9	10% alcohol
0.01	0.2420	0.2319	−4.2	50% alcohol
0.01	0.2420	0.2352	−2.8	1% acetic acid
0.01	0.2420	0.2312	−4.5	10% alcohol + 1% acetic acid
0.01	0.2420	0.2307	−4.7	30% alcohol + 1% acetic acid
0.01	0.2420	0.2168	−10.4	50% alcohol + 1% acetic acid
		LITHIUM SULFATE		
0.1	2.180	2.158	−1.0	Water[a]
0.1	2.180	2.148	−1.5	Water[b]
0.1	2.180	2.163	−0.8	Water[b,e]
0.1	2.180	2.143	−1.7	10% alcohol[a]
0.1	2.180	2.135	−2.0	10% alcohol[b]
0.1	2.180	2.138	−1.9	10% alcohol[b,e]
0.1	2.180	2.168	−0.5	1% acetic acid[a]
0.1	2.180	2.143	−1.7	1% acetic acid[b]
0.1	2.180	2.148	−1.5	1% acetic acid[b,e]
0.01	0.2180	0.2170	−0.6	1% acetic acid
0.01	0.2180	0.2178	−0.1	1% acetic acid[a,e]
0.01	0.2180	0.2073	−4.9	50% alcohol + 1% acetic acid[a]
0.01	0.2180	0.2073	−4.9	50% alcohol + 1% acetic acid[a,e]
0.01	0.2180	0.2138	−1.9	Water[a]
0.01	0.2180	0.2138	−1.9	Water[c]
0.1	0.2180	0.2153	−1.2	Water[c,e]
0.01	0.2180	0.2128	−2.4	10% alcohol[c]
0.01	0.2180	0.2113	−3.1	10% alcohol[d,e]
0.01	0.2180	0.2098	−1.9	30% alcohol[d]
0.01	0.2180	0.2098	−1.9	30% alcohol[d,e]
0.01	0.2180	0.2154	−1.0	50% alcohol[d]
0.01	0.2180	0.2148	−1.5	50% alcohol[d,e]
0.001	0.0215	0.0219	+1.6	20% alcohol[d]
0.001	0.0215	0.0219	+1.6	20% alcohol[d,e]
0.001	0.0215	0.0222	+3.0	30% alcohol[d]
0.001	0.0215	0.0222	+3.0	30% alcohol[d,e]
		ZINC SULFATE		
0.05	1.250	1.173	−6.1	Water
0.05	1.250	1.189	−4.9	10% alcohol
0.05	1.250	1.206	−3.5	20% alcohol
0.05	1.250	1.230	−2.0	30% alcohol
0.05	1.250	1.254	0.0	40% alcohol
0.05	1.250	1.274	+1.9	50% alcohol
0.05	1.250	1.198	−4.1	1% acetic acid
0.05	1.250	1.211	−3.1	10% alcohol + 1% acetic acid
0.05	1.250	1.224	−2.0	30% alcohol + 1% acetic acid
0.05	1.250	1.236	−1.1	50% alcohol + 1% acetic acid
0.005	0.1250	0.1212	−3.0	Water
0.005	0.1250	0.1218	−2.6	10% alcohol
0.005	0.1250	0.1216	−2.7	20% alcohol
0.005	0.1250	0.1206	−3.5	30% alcohol
0.005	0.1250	0.1193	−4.5	40% alcohol
0.005	0.1250	0.1156	−7.6	50% alcohol
0.005	0.1250	0.1255	+0.4	1% acetic acid
0.005	0.1250	0.1243	−0.6	10% alcohol + 1% acetic acid
0.005	0.1250	0.1209	−2.3	30% alcohol + 1% acetic acid
0.005	0.1250	0.1150	−8.0	50% alcohol + 1% acetic acid

[a] Reading after 3 minutes.
[b] Reading after 30 minutes.
[c] Reading after 15 minutes.
[d] Reading after 5 minutes.
[e] Shaken.

The angle between the precipitation line and the reagent line is much more obtuse in the titrations of zinc sulfate than in that of alkaline sulfates which makes the titration less precise (compare Figure 1). It could be expected that in the titration of more dilute sulfate solutions, the difference due to the different cations would disappear or decrease. Still more marked differences were found in the titration of 0.01 N alkali and zinc sulfate solutions. The titration of 0.01 N potassium sulfate yields results which are about 3.5 per cent low. The procedure is not very pleasant with water as a solvent because a fairly long time is required before the conductivity ceases to change on standing. In the presence of alcohol constant readings are obtained much sooner, whereas alcohol itself has little effect upon the results. It is recommended that not more than 30 per cent alcohol be

added. In the presence of alcohol and acetic acid the results are much too low, especially when the alcohol concentration is larger than 40 per cent. The titration of 0.01 N sodium sulfate gives results which are about 2 per cent low. Addition of alcohol, or alcohol with 1 per cent acetic acid, has qualitatively the same effect as described for potassium sulfate. With lithium sulfate, approximately the same results

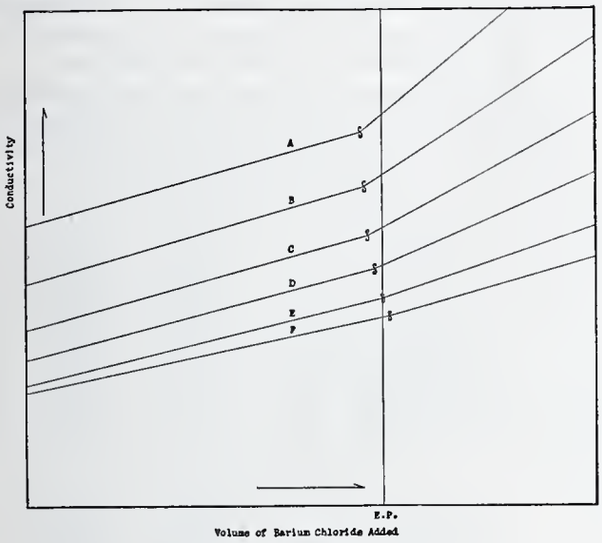


Figure 1—Titration of Zinc Sulfate with Barium Chloride

A, aqueous solution
B, 10% alcohol solution
C, 20% alcohol solution
D, 30% alcohol solution
E, 40% alcohol solution
F, 50% alcohol solution

are found as with 0.01 N sodium sulfate. Comparable results are obtained in the titration of 0.005 N zinc sulfate solutions. When the concentration of the alcohol present is not larger than 30 per cent, the error is about −3 per cent; with more alcohol, the deviation increases rapidly (in 50 per cent alcohol about 7 per cent). It is peculiar that even in the titration of 0.005 N zinc sulfate, the angle between the precipitation line and reagent line is so much more obtuse than in the titration of 0.01 N alkali sulfate. Addition of alcohol makes the angle still more obtuse. As an example, Figure 1 represents the titration lines of zinc sulfate with barium chloride in water and different concentrations of alcohol. The straight line drawn through *E. P.* indicates the location of the equivalence point (theoretical end point). The slope is about the same for 0.05 N as for 0.005 N solutions. (Compare the angle with that in Figures 3 and 5, where titration lines of alkali sulfates are given.) Finally, the titration of very dilute sulfate solutions of the order of 0.001 N (46 mg. SO_4 in a liter) was examined. There, of course, the gravimetric method is a very painstaking procedure and the conductometric method gains special significance. In the absence of alcohol the titration is very impracticable; it takes too long a time before the conductivity is constant after addition of reagent. In the presence of 20 to 30 per cent alcohol, the results obtained were about 1.5 to 3 per cent high and quite well reproducible. In Figure 2 is shown the titration curve of 0.001 N lithium sulfate in 30 per cent alcohol. For the estimation of the sulfate content of very dilute solutions which do not contain relatively large amounts of other electrolytes, the conductometric method is the best and yields results which are more reliable and better reproducible than those obtained by the nephelometric method. Quite generally, it is recommended to add not more than 30 per cent alcohol. With more alcohol the precipitate often has a tendency to enter into colloidal solution, especially with an excess of barium.

Interpretation of Results

As we have seen above, the knick point is always found before the equivalence point, the error being especially large in the titration of 0.1 N potassium sulfate and zinc sulfate. Of course, one would feel very strongly inclined to attribute the low results to a coprecipitation of alkali or zinc sulfate with the barium sulfate. The occlusion of potassium and zinc, especially, should be very large in this case. However, the following experiments show that coprecipitation does not account for the low results.

To different portions of 50 cc. 0.1 N potassium sulfate, normal barium chloride was added corresponding to 95, 96, 97, 98, 99, 100, and 101 per cent of the equivalent amount. After standing, the mixtures were filtered and the filtrates tested with more barium chloride. A decreasing cloudiness was observed in the first five filtrates, but even the filtrate of the mixture to which 99 per cent barium chloride had been added still contained some sulfate, whereas after addition of 100 per cent, the filtrates were sulfate-free. With zinc sulfate, another type of experiment has been made. About 10 per cent excess of barium chloride was added to the 0.1 N solution, the precipitate collected, and washed with water until free of barium. The zinc content in the filtrate was determined by the simple and accurate gravimetric *o*-oxyquinoline (oxin) method and a recovery of exactly 100 per cent, ±0.5 per cent, was found. Hence, there was no coprecipitation of zinc sulfate or zinc oxide (hydrolytic adsorption) with the barium sulfate. In other experiments, separate portions of 50 cc. 0.1 N zinc sulfate were added to 95, 97, 99, 100, 101, and 110 per cent of the equivalent amount of barium chloride; the precipitates were collected, washed out, and weighed. The weights found corresponded to 95.3, 97.7, 99.0, 100.1, 100.0, and 99.5 per cent precipitation. These experiments show quite conclusively that coprecipitation is not responsible for the low results of the conductometric titrations.

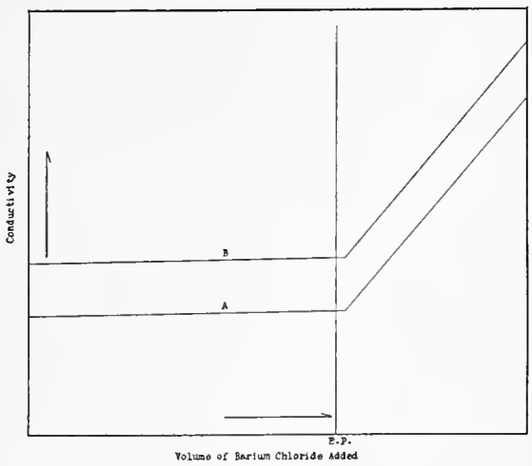


Figure 2—Titration of 0.001 N Lithium Sulfate with 0.1 N Barium Chloride

A, 5 minutes after addition of solution
B, shaken after *A*

In the titration of potassium sulfate with barium chloride, the sulfate is replaced by the chloride ion until the equivalence point has been reached. In order to be sure that the line which represents the conductivity of mixtures of 0.1 N potassium sulfate and chloride, respectively, had no irregular shape, it has been determined experimentally. Though the line is not quite straight, the deviation is so small that it cannot account for the displacement of the knick point in the conductivity titrations. Therefore, the remaining possibility of explaining the deviations found in the conductometric titrations is that the presence of the precipitate itself

affects the readings of the conductivity. Moreover, we have to consider the adsorbent properties of barium sulfate. When precipitated from a sulfate solution, the precipitate will have a negative charge as long as there is an excess of sulfate due to some adsorbed alkali sulfate on the surface. This adsorption will decrease the more we approach the equivalence point and will be about zero at that point. The precipitate will then have a tendency to adsorb barium ions (and acquire a positive charge) with an excess of reagent. That freshly precipitated barium sulfate has a tendency to adsorb barium ions could be proved experimentally. It even seems that the barium ion is much more strongly adsorbed

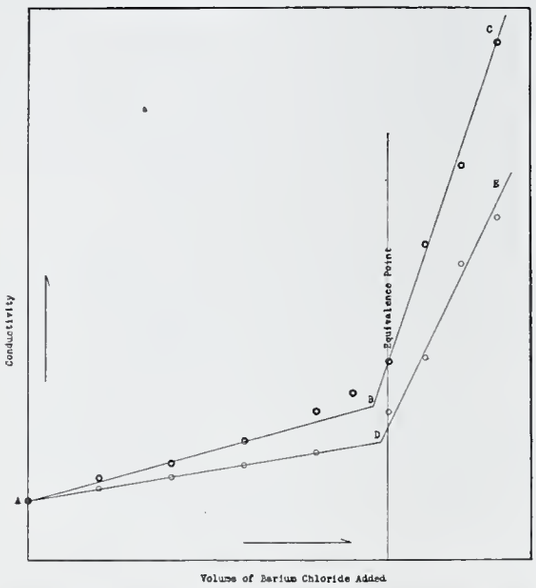


Figure 3—Titration of Potassium Sulfate with Barium Chloride

ABC, measurement taken in presence of barium sulfate
ADE, measurement taken with filtrate

than the sulfate ion; with an excess of the latter ion, there is no difficulty in getting a clear filtrate; with an excess of barium, however, the filtrate is usually cloudy and it requires a very dense filter to obtain a clear filtrate. Moreover, if there is 40 to 50 per cent alcohol present, the precipitate shows a strong tendency to go into a colloidal suspension.

The barium sulfate precipitated at room temperature consists of very fine particles; on standing, the size probably increases and the adsorption decreases. For this reason, somewhat better results may be expected if the conductivity is measured after some time of standing. If the barium sulfate contains some sulfate or barium adsorbed at its surface, the charged particles will show some conductance of the electric current when suspended in the solution. Therefore, it could be expected that the knick point would be found much nearer the equivalence point when the conductivity was measured in a clear solution from which the precipitate had settled or had been removed by filtration. Special experiments were conducted to study the influence of the precipitate. As a matter of fact, the following experiments have no direct analytical significance as the technic is very impracticable; the results, however, may contribute to an understanding of the error in the direct titration of sulfate with barium chloride. Potassium sulfate 0.1 *N* was titrated with 1 *N* barium chloride. The conductivity was measured 3 and 10 minutes, respectively, after addition of the reagent. Moreover, readings have been made after 10 minutes' standing and after stirring up the precipitate. Four sets of determinations have been made. In some cases the points representing the conductivity data deviated less from a straight line than other cases. Under the different conditions mentioned, the knick point was found 4.5 to 6 per cent before the equivalence point.

Four sets of determinations have been made, in which the points of the precipitation and reagent line were determined in the filtrate. Sometimes it was very difficult to get a clear filtrate. Moreover, great care has to be taken that no evaporation occurs during filtration. If the precipitate has no influence upon the conductivity, we might expect that the slope of the precipitation and reagent line would be the same in the filtrate as in the direct titration. Actually it was found that in the filtrates the slope of the precipitation line and, to a lesser extent, of the barium chloride line, is much less than in the direct titrations without filtrations.

This shows conclusively that the conductivity is higher in the presence of the precipitate than in the filtrates. The more barium sulfate present, the larger the difference between the reading in the unfiltered and filtered solutions. It may be that at the equivalence point the charge is due to adsorbed alkali chloride. In Figure 3, *ABC* represents the change in conductivity in the direct titration (measurements after 3 and 10 minutes, respectively), whereas *ADE* shows the precipitations and reagent line as measured in the filtrate. In the latter case, the knick point is found much nearer the equivalence point, the deviation being now of the order of 1 to 2 per cent. In order to confirm the results, a set of readings has been made with mixtures of potassium sulfate and potassium chloride of the same composition as could be expected in the filtrate. The slope of this line coincides with that of the precipitation line in the filtrate. The higher conductivity in the presence of the barium sulfate cannot be attributed to

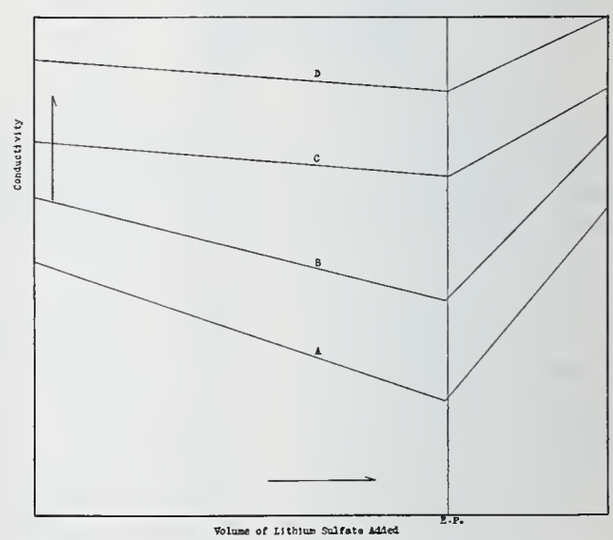


Figure 4—Titration of Barium Chloride with Lithium Sulfate

A, aqueous solution
B, 10% alcohol solution
C, 30% alcohol solution
D, 50% alcohol solution

its solubility as the latter is very small and moreover has the same value in the filtrates. The only facts to account for the irregularities and deviation in the presence of the precipitate are that the barium sulfate increases the conductivity of the solution because of its charge, and that the cell constant may be affected more or less by the presence of the suspended particles.

Titration of Barium Chloride with Sulfates

The results of the titration of barium chloride with sulfates are reported in Table II.

In the titration of 0.1 *N* barium chloride with an *N* sulfate solution, the knick point is found ±1 per cent before or after the equivalence point. With potassium sulfate as a reagent, the deviation was about +1 per cent, with sodium sulfate −1.5 per cent, and with lithium sulfate −0.5 per cent. There-

fore, the mutual agreement is much better and the knick point much closer to the equivalence point than in the reverse titration of the different alkali sulfates with barium chloride. From the last two sections of Table II we see that addition of alcohol shifts the knick point more to the right, resulting in a larger error. With 50 per cent alcohol as a solvent, the deviation was +5 per cent using sodium sulfate as a reagent. One per cent acetic acid and especially the combination of alcohol and acetic acid have a tendency to increase the deviation still more.

Table II—Titration of Barium Chloride with Sulfates

Barium Concn.	Amount Taken	Barium Found	Deviation	Solvent
N	*Millimols*	*Millimols*	%	
		POTASSIUM SULFATE		
0.1	2.514	2.541	+1	Water
0.1	2.514	2.566	+2	10% alcohol
0.1	2.514	2.640	+5	10% alcohol + 1% acetic acid
0.01	0.2503	0.2539	+1.4	Water
0.01	0.2503	0.2569	+2.6	10% alcohol
0.01	0.2503	0.2559	+2.2	20% alcohol
0.01	0.2503	0.2554	+2.0	30% alcohol
0.01	0.2503	0.2564	+2.4	40% alcohol
0.01	0.2503	0.2554	+2.0	50% alcohol
0.01	0.2503	0.2554	+2.0	1% acetic acid
0.01	0.2503	0.2564	+2.4	10% alcohol + 1% acetic acid
0.01	0.2503	0.2600	+3.8	20% alcohol + 1% acetic acid
0.01	0.2503	0.2637	+5.4	40% alcohol + 1% acetic acid
		SODIUM SULFATE		
0.1	2.514	2.476	−1.5	Water
0.1	2.514	2.572	+2.1	10% alcohol
0.1	2.514	2.642	+5.1	50% alcohol
0.1	2.514	2.572	+2.3	1% acetic acid
0.1	2.514	2.567	+2.1	10% alcohol + 1% acetic acid
0.1	2.514	2.688	+6.9	50% alcohol + 1% acetic acid
0.01	0.2503	0.2509	+0.2	Water
0.01	0.2503	0.2514	+0.5	10% alcohol
0.01	0.2503	0.2552	+2.0	20% alcohol
0.01	0.2503	0.2586	+3.3	50% alcohol
0.01	0.2503	0.2528	+1.0	1% acetic acid
0.01	0.2503	0.2562	+2.3	10% alcohol + 1% acetic acid
0.01	0.2503	0.2567	+2.6	20% alcohol + 1% acetic acid
0.01	0.2503	0.2586	+3.3	50% alcohol + 1% acetic acid
		LITHIUM SULFATE		
0.01	0.2503	0.2486	−0.7	Water[a]
0.01	0.2503	0.2490	−0.5	Water[b]
0.01	0.2503	0.2486	−0.7	10% alcohol
0.01	0.2503	0.2486	−0.7	10% alcohol[b]
0.01	0.2503	0.2505	+0.1	30% alcohol
0.01	0.2503	0.2505	+0.1	30% alcohol[b]
0.01	0.2503	0.2503	0.0	50% alcohol
0.01	0.2503	0.2503	0.0	50% alcohol[b]
0.01	0.2503	0.2473	−1.2	1% acetic acid
0.01	0.2503	0.2477	−1.0	1% acetic acid[b]
0.01	0.2503	0.2542	+1.5	50% alcohol + 1 % acetic acid
0.01	0.2503	0.2551	+1.9	50% alcohol + 1% acetic acid[b]
0.001	0.0252	0.0239	−5.3	10% alcohol
0.001	0.0252	0.0239	−5.3	10% alcohol[b]
0.001	0.0252	0.0243	−3.5	20% alcohol
0.001	0.0252	0.0244	−3.1	20% alcohol[b]
0.001	0.0252	0.0244	−3.3	30% alcohol
0.001	0.0252	0.0244	−3.3	30% alcohol[b]
0.001	0.0252	0.0245	−2.8	50% alcohol
0.001	0.0252	0.0245	−2.8	50% alcohol[b]

[a] Reading taken after 5 minutes.
[b] Shaken.

In the titration of 0.01 *N* barium chloride with any of the three alkali sulfates, theoretical results are found within 1 per cent. It is practicable to add some alcohol if we are dealing with 0.01 *N* or more dilute solutions, as the conductivity then soon becomes constant after addition of the reagent. In concentrations lower than 30 per cent, the alcohol has almost no influence upon the location of the knick point. The same holds for the combination of 1 per cent acetic acid and alcohol if the concentration of the latter is lower than about 30 to 40 per cent.

Of special practical significance again is the conductometric titration of very dilute barium solutions of the order of 0.001 *N*. In the presence of 30 to 40 per cent alcohol, the results are quite reproducible though the knick point appears about 3 per cent before the equivalence point.

It is interesting to note that the angle between the precipitation and reagent line becomes more obtuse with increasing alcohol content of the medium, especially the slope of the

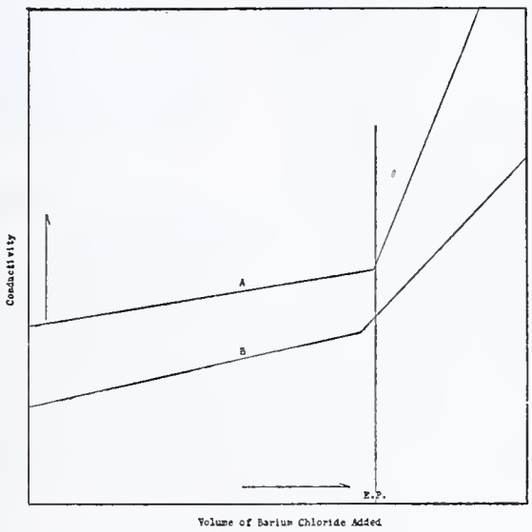


Figure 5—Titration of Lithium Sulfate with Barium Chloride

A, 1% acetic, 50% alcohol solution
B, 1% acetic acid solution

precipitation line where the barium is replaced by the alkali ion, which is much less in the presence of alcohol. The effect is very much pronounced, as may be seen in Figure 4. Here the change of conductivity in the titration of 0.01 *N* barium chloride in water, 10, 30, and 50 per cent alcohol, respectively, with lithium sulfate is represented. On the other hand, in the titration of sulfate solutions, alcohol has very little influence upon the slope of the precipitation line, whereas the slope of the reagent (barium chloride) line is much flatter in the presence of alcohol. This is shown in Figure 5, where lines are given for the titration of 0.01 *N* lithium sulfate in water and 50 per cent alcohol, respectively, with barium chloride.

From these phenomena, it may be inferred that the mobility of the barium ions is much more decreased by alcohol than that of the alkali chloride and sulfate ions. Whereas the mobility of the barium ions in water is much larger than that of the sodium ion, the difference between the two is very small in 50 per cent alcohol.

Literature Cited

(1) Dutoit, P., *J. chim. phys.*, **5**, 27 (1910); for literature review compare I. M. Kolthoff, "Konduktometrische Titrationen," p. 69, Steinkopff, Dresden, 1923.
(2) Jander, G., and Pfundt, O., "Die visuelle Leitfähigkeitstitration," p. 32, Verlag Enke, Stuttgart, 1929.
(3) Kolthoff, I. M., Ind. Eng. Chem., Anal. Ed., **2**, 225 (1930).

World's Largest Ultra-Violet Plant Installation—What is believed to be the largest installation of equipment for the production of ultra-violet rays in any industrial plant is that of the American Tobacco Company in its Richmond, Va., works. The installation is unique in that it is adapted to the proper unit process and the process has not been changed to conform to the installation.

The great banks of ultra-violet light-producing units require for their operation 45 horsepower per hour. Each unit consists of 12 arc lamps, each requiring 60 amperes at 50 volts across the arc. The top carbons are 0.875 inch in diameter; those at the bottom, 0.50 inch; and a grade of cored carbons, designated as "C carbons," which give the most ultra-violet light, are those employed. Similar units are in operation at their Reidsville and Durham plants. Five and one-half units are required for this operation in all of their plants.

Determination of Lead as Chromate in Presence of Perchloric Acid[1]

D. J. Brown, Joseph A. Moss, and John B. Williams

University of Nebraska, Lincoln, Neb.

Lead may be precipitated rapidly and quantitatively as chromate from dilute solutions of perchloric acid.

Lead may be determined volumetrically by using a standard dichromate solution for the precipitation and then determining the excess by a residual titration iodometrically.

THE facts here presented indicate that a solution of lead in the presence of perchloric acid may be prepared readily and that lead may be precipitated more nearly quantitatively and more quickly as chromate from such a solution than by the methods in common use at present.

Preliminary semi-quantitative observations showed that lead chromate is less soluble in diluted solutions of perchloric acid than in solutions of nitric or hydrochloric acid of the same normality (*3*), and especially so if alkali salts of these acids were also present but, compared to lead chromate, other chromates are very soluble. Also the lead chromate, when precipitated hot with dichromate solution, clarifies the solution as soon as an excess of the precipitant is present and the precipitate is in a readily filterable form. This is not true for the precipitate from the commonly used acetate solution. Hydrochloric acid is readily volatilized from concentrated solutions of perchloric acid before the formation of fumes due to perchloric acid. Also, as found by Willard and Coke (*2*), silica is very insoluble when heated with perchloric acid.

The details of the methods in their final form are as follows.

Gravimetric Method

Treat the ore with hydrochloric acid, adding a little nitric acid if necessary, as is usually done. Evaporate almost to dryness. Add 10 to 15 cc. of 6 per cent perchloric acid and evaporate almost to dryness. Dilute, filter, and wash. The final volume should be about 200 cc. Heat to 70° C. and add a diluted dichromate solution slowly while stirring until the color of the solution is that of 5 to 20 cc. of 0.1 *N* dichromate in the same volume. Allow to cool. Filter through a Gooch crucible and wash with a minimum amount of water that has been slightly acidified with perchloric acid.

Place the Gooch crucible within an asbestos ring so that at least a third of the crucible is below the asbestos. Place on top of a 3-inch iron crucible. Raise the temperature gradually until the iron crucible is red-hot. Continue to heat an hour and then allow to cool.

Volumetric Method

To precipitate the lead chromate as given under the gravimetric method, use 0.1 *N* dichromate. This may be prepared by direct weighing of the calculated amount of the dried potassium dichromate and checked by standardizing against a lead solution by the method given below.

To the cold filtrate from the lead chromate add 25 to 30 cc. of 6 per cent perchloric acid and 3 grams of potassium iodide, allow to stand a few minutes, then titrate with 0.1 *N* thiosulfate (*1*).

To standardize the solution against lead, titrate the dichromate solution with the 0.1 *N* thiosulfate and after precipitating a known amount of lead, calculate the strength using a hydrogen equivalent of 3 for the lead.

Experiments

The best grade reagents easily obtained were used to prepare all solutions.

To test the method, a lead solution was prepared from silver-free lead similar to the method for the dissolving of the ore, each cubic centimeter of which would yield 0.01616 gram of lead chromate.

The 0.1 *N* barium chloride was prepared by dissolving the calculated amount of the salt.

The 6 per cent perchloric acid solution was prepared by diluting the 60 per cent perchloric acid to 10 volumes.

The acidified water was prepared by diluting the preceding solution to 10 volumes.

Ten 40-cc. portions of the lead solution were analyzed, 10 cc. of 6 per cent perchloric acid being used in each case. The average weight was 0.1 mg. high. The maximum variation was ±0.2 mg., except one portion which was 0.4 mg. high.

Since barium chromate is the least soluble of the other possible interfering chromates, 15 portions of the same size, etc., as the preceding, except that the solution contained also 5 cc. of 0.1 *N* barium chloride, were analyzed. The average of all was the theoretical. Twelve values showed a variation from this of ±0.3 mg. The others were greater but less than 1 mg.

Another series was run similar to the preceding except that 10 cc. of 0.1 *N* barium chloride and 15 cc. of 6 per cent perchloric acid were used. The average results were 0.04 per cent low, but the maximum variation from the mean theoretical value was −0.7 mg., and the minimum −0.2 mg. This indicates probably the maximum permissible concentration of the perchloric acid.

Several different ores have been analyzed. For example, fifteen portions of approximately a half gram each of a lead ore that had been analyzed by the Bureau of Standards were analyzed. Except for some spattering, there were no undesirable features. The results for which we secured values by both methods are given in Table I.

Table I—Analyses of Lead Samples by Gravimetric and Volumetric Methods

Sample	Gravimetric			Volumetric		
	Lead chromate	Lead		Potassium dichromate[a]	Lead	
Gram	*Gram*	*Gram*	%	*Cc.*	*Gram*	%
0.5010	0.6388	0.4095	81.76	36.18	0.40935	81.71
0.5035	0.6426	0.4119	81.80	36.20	0.41185	81.80
0.4996	0.6366	0.4081	81.70	36.06	0.40805	81.68
0.5053	0.6447	0.4133	81.78	36.52	0.41225	81.58
0.4985	0.6365	0.4080	81.84	36.06	0.40805	81.85
0.4997	0.6375	0.4087	81.76	36.10	0.40845	81.71
0.5110	0.6528	0.4185	81.71	36.98	0.41845	81.88
0.5054	0.6455	0.4138	81.86	36.56	0.41365	81.82
0.4905	0.6268	0.4019	81.92	35.50	0.40165	81.86
0.5121	0.6534	0.4189	81.80	37.02	0.41885	81.79
0.5017	0.6398	0.4102	81.76	36.38	0.41165	82.04
0.5142	0.6545	0.4196	81.60	37.06	0.41935	81.55
		Av.	81.77		Av.	81.77

[a] 1 cc. potassium dichromate = 0.011315 ± 0.00005.

[1] Received October 21, 1930.

The value of the ore was 81.69 per cent according to the Bureau of Standards.

Several samples of the ore were treated with hydrochloric acid, etc., without removing the residue, filtered hot, the iodide added at once, and the whole titrated. The results were 0.2 to 0.7 per cent high. If the solutions are standardized under the same conditions as the titration, the results are almost as accurate as those given above. However, for a quick method where greater accuracy is not required, this should be satisfactory.

Literature Cited

(1) Treadwell and Hall, "Analytical Chemistry," Vol. II, 7th ed., p. 554, Wiley, 1928.
(2) Willard and Coke, *J. Am. Chem. Soc.*, **42**, 2208 (1920).
(3) Willard and Kassner, *Ibid.*, **52**, 2402 (1930). This work was completed before their paper was published.

Measurement of Color in Solutions of White Sugars[1,2]

J. A. Ambler and S. Byall

Bureau of Chemistry and Soils, Washington, D. C.

The measurement of the colors of white sugars was placed on a reproducible, accurate basis by matching the colors of water solutions of the sugar against a standard caramel solution made by diluting Balch's No. 5 maple sirup color standard solution. For the determination of color of hard candies made from the sugars, the candies were dissolved in water and the colors of the solutions matched against a diluted No. 9 maple sirup color standard solution. The color of the barley candy is not related to the color of the original white sugar.

THE grading of white sugars by the color of their solutions has been done in the past by means of more or less arbitrary methods which lack any exact meaning in terms of the absolute quantity of coloring matter present. For solutions of white sugars, grading by means of Stammer degrees is not satisfactory because of the extreme paleness of the colors encountered. In grading the sugars produced during a campaign, or in comparing the colors of sugars of different yearly campaigns, some reproducible standard is necessary if reliable comparisons are desired. This is now possible by use of standards adapted from the color standards for maple sirup as defined by Balch (*2*), who has worked out exact specifications for obtaining reproducible caramel solutions of given depth of color. These standard specifications are based on the amount of light transmitted by the caramel solution at 560 mμ.

Since the color of most white sugars is caused by occluded and adhering films of the colored liquor from which the sugar crystallized, it is in most cases very similar to that of caramel, especially in the paler shades generally encountered. In only a comparatively few cases does the color assume a grayish or greenish hue. When such abnormally colored sugars are found it is impossible to grade them with the normal-colored ones by any method short of complete spectroanalysis. In many cases the grayness of a sugar is caused by particles of dust or of carbon which have not been eliminated by filtration or which may have accidentally become admixed with the sugar during the final stages of drying and sacking. If these particles are removed from the solutions it will often be found that a gray sugar will yield a normal-colored sirup.

The method here described was used satisfactorily during the past year in grading samples of white sugar collected from various factories, and also in grading the color of the hard barley candies made from them by the standard hard candy test (*1*).

The standard color solution for the sugar solutions was made from Balch's No. 5 maple sirup color standard solution by taking 10 grams and diluting it with water to 100 cc. This was placed in one side of a colorimeter, in this case one of the Campbell-Hurley type, although other types would be equally serviceable. A solution of the sugar to be graded was prepared by dissolving 120 grams in water, making up to 200 cc., adding 15 to 20 grams of Filter-Cel, and, after thorough mixing, filtering through paper on a Büchner funnel. The clear filtrate was placed in the other side of the colorimeter and the color determined by finding the volume of the standard solution necessary to match exactly the color of 100 cc. of the filtered sugar solution. Uniform light source was assured by making the readings in a dark room and using a daylight lamp to illuminate the solutions. This method of reading gives a direct measure of the amount of coloring matter present; the deeper the color, the greater the number obtained. If a sugar solution is darker than the standard, the color of 50 cc. (or, if necessary, of 25 cc.) of the unknown may be matched against the standard, and the reading obtained is then to be multiplied by 2 (or by 4) to make the determination comparable with the rest of the series.

For measuring the color of the barley candies it seemed desirable, though it is not absolutely necessary, to use a stronger standard and a more dilute solution of the candy because of the deeper color of the candies. Accordingly a No. 9 Balch maple sirup color standard solution was diluted exactly as before (10 grams to 100 cc.) and measured against a filtered solution of 30 grams of the candy made up to 200 cc. with water. The use here of a stronger standard and a weaker candy solution obviates the necessity of using more than 100 cc. of the standard solution.

This method is flexible and susceptible of various modifications as the exigencies of the work require. For example, by using the same standard, it is possible to estimate the increase of color occurring during storage of sugar, or during boiling or concentration of sirups or liquors. The color may be expressed on the basis of total dry solids, total sugars, total non-sugars, or any other desired basis. For the grading of white sugars, direct readings are sufficient, since the figures obtained by calculating to a total solids or a total sugar basis are directly proportional to the readings found, because the quantity of impurities present in the white sugar is proportionately smaller than that of the experimental error.

If desired, the readings may by proper calculations be converted to percentage transmittancy or to extinction coefficient, since Balch's standards are based on the percentage transmittancy, from which the extinction coefficients may readily be derived.

A few of the results obtained are shown in Table I.

[1] Received October 30, 1930. Presented before the Division of Sugar Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Contribution No. 99, Carbohydrate Division, Bureau of Chemistry and Soils.

Table I

Sugar	Color	Color of Candy[a]	Sugar	Color	Color of Candy[a]
	%	%		%	%
a	85	41	*h*	166	Not detd.
b	55	50	*i*	200	47
c	50	42	*j*	198	60
d	45	40	*k*	60	24
e	78	120	*l*	92	25
f	42	39	*m*	71	83
g	100	85	*n*	85	36

[a] Stronger standard and more dilute solution used.

From these values of the color in the sugar and in the candy it is evident that the color of the sugar has no definite relation to the color of the candy produced from the sugar, and consequently there is no need of using the same standard color solutions in grading the sugar and the candy. The only comparisons that may be drawn are those between the sugars themselves and those between the candies themselves.

Literature Cited

(1) Ambler, *Manufacturing Confectionery*, **7**, No. 1, 17 (1927).
(2) Balch, Ind. Eng. Chem., **22**, 255 (1930).

Impurities in White Sugars

I—Determination of Phosphorus[1,2]

S. Byall and J. A. Ambler

Bureau of Chemistry and Soils, Washington, D. C.

The importance of traces of impurities in sugar is being recognized more and more, necessitating the development of methods of analysis of greater sensitivity. Inorganic and organic phosphorus compounds which are present in the plant find their way into the juices and eventually into the white sugars crystallized from these juices. The Briggs modification of the Bell-Doisey coerulo-molybdate method of determining phosphates is sufficiently delicate to show the amounts of inorganic phosphorus and, by difference, will show the amounts of organic phosphorus present in sugar. The test is capable of showing as little as 0.3 p.p.m. P_2O_5 when applied to a 10-gram sample. Analyses of a large number of white sugars of all kinds have revealed the fact that organic phosphorus compounds are not entirely eliminated by modern methods of sugar production.

It is common knowledge among sugar chemists and technologists that in evaluating white sugars for certain uses the ordinary gravimetric, volumetric, and physical chemical methods of analysis are inadequate. For example, two samples of white sugar may be practically indistinguishable when examined for ash, invert sugar, sucrose, pH, color, turbidity, and so forth, and yet one sample may show a greater tendency toward caramelization on heating or may be more susceptible to fermentation than the other. Such differences in behavior must be caused by impurities which are present in quantities so minute that either they have been formerly considered unimportant and therefore not determined, or they are capable of estimation only by special methods of a sensitivity greater than that of the methods in general use.

In studying the causes of such differences in behavior, the first point of attack is from the analytical end. Only when the amounts of the impurities are known is it possible, by adding appropriate quantities of each to pure sucrose, to determine from any desired viewpoint the effect of each foreign substance and of combinations of them. The determination of the quantities of contaminants which are present only in traces is often difficult, not only because of the lack of methods of sufficient sensitivity but also because of the extreme reactivity of sucrose itself toward chemical reagents. Therefore, it is necessary to devise methods or to modify existing methods so as to increase their sensitivity and overcome interference by the sugar. Several such methods have been worked out and will be the subjects of the first part of a series of publications on the "Impurities in White Sugars." The effects of these impurities will be discussed later in the series.

Although in dealing with traces of organic substances it is rarely possible in the present state of knowledge even to detect the presence of an individual organic compound, it is very often possible to determine the total quantity of a group of compounds having in common some characteristic reaction or atomic grouping. The ninhydrin test for amino acid compounds (*1*) is a group test of this character, since it is specific for no individual amino acid, polypeptide, or other hydrolytic product of albumin, but is given by the class of compounds which contain an amino group in the alpha position to a carboxyl group. With the refinement of analytical methods and technic it may eventually be possible to subdivide such groups of related compounds into smaller ones, or in some cases to determine chemical individuals.

Phosphorus Compounds in White Sugars

It has long been known that phosphates are present in the juices of the sugar cane and of the sugar beet. In the processes of manufacture of sugar, the lime which is added in the clarification of the juice combines with the phosphates present to form the relatively insoluble calcium phosphates. But because the latter are appreciably soluble, a small quantity of inorganic phosphates always remains in the liquors and, as will be shown, may often be determined in the white sugar.

Organic phosphorus compounds such as lecithin and the nucleic acids also occur in the tissues of the sugar cane (*5*) and of the sugar beet (*4*). They will therefore pass into the mill and diffusion juices and will be subjected to the action of lime in the clarification. The lecithins on treatment with alkalies yield among their hydrolytic products glycerophosphoric acid which, on account of the solubility of its calcium salt (*6*), will be removed from the liquors only to the extent that it is adsorbed by the compounds precipitated in the sludge. The nucleic acids are more stable toward lime than the lecithins and probably are hydrolyzed to a less extent during the processes of sugar making. Neither type of these phosphorus compounds responds to the ordinary tests for phosphates until the organic portion of their molecules has been destroyed or removed by hydrolysis. The occurrence of organic phosphorus in white sugars has not

[1] Received November 28, 1930.
[2] Contribution No. 105, Carbohydrate Division, Bureau of Chemistry and Soils.

been reported in the literature, so far as the authors are aware. By using the method to be described, the quantity of organic phosphorus is found generally to exceed that of the inorganic phosphorus.

Because of the extremely small quantity of phosphorus in the sugar, it is not feasible to use any of the ordinary gravimetric or volumetric methods of determining it. This was clearly indicated by preliminary experiments in which it was necessary to use samples of sugar weighing several hundred grams in order to obtain sufficient phosphate for gravimetric determination. These attempts showed, however, that the proportion of total phosphorus (obtained by wet oxidation with nitric acid whereby all organic matter was destroyed) was best expressed in terms of parts per million of sugar. The Briggs (*3*) modification of the Bell-Doisey (*2*) colorimetric method for phosphates was found to be rapid and economical. Sucrose does not interfere with the development of the color. The test is specific for inorganic phosphates and therefore lends itself to the differentiation of organic and inorganic phosphorus compounds. It is sufficiently sensitive to allow of easy determination of 0.003 mg. of P_2O_5, or, in a 10-gram sample of sugar, of 0.3 p. p. m.

The reagents used are as follows:

Standard Phosphate Solution—A sample of potassium dihydrogen phosphate weighing 0.4394 gram is dissolved in water and diluted to one liter. Twenty-five cc. of this solution are then diluted to 200 cc. This gives a solution which contains 0.02866 mg. of P_2O_5 per cubic centimeter.

Molybdate Solution—Twenty-five grams of ammonium molybdate are dissolved in 300 cc. of water and to this are added 200 cc. of water containing 75 cc. of concentrated sulfuric acid.

Hydroquinone Solution—Half a gram of hydroquinone is dissolved in 100 cc. of water to which a drop of sulfuric acid has been added to retard oxidation.

Sulfite Solution—Twenty grams of sodium sulfite are dissolved in 100 cc. of water. The solution should be freshly prepared.

Nitric Acid—One volume of concentrated nitric acid is diluted with an equal volume of distilled water.

Preparation of Colorimetric Standards—The standards for the colorimetric comparison are developed simultaneously with the unknowns. Measured volumes ranging from 0.1 to 10.0 cc. of the standard phosphate solution are placed in 100-cc. Nessler tubes. To each are added, in the order given, 5 cc. of the molybdate solution, 1 cc. of the sulfite solution, 1 cc. of the hydroquinone solution, and enough distilled water to make a final volume of 100 cc. The solutions are mixed and allowed to stand for 30 minutes. Standard solutions made up with and without the addition of pure sucrose showed no difference in hue or depth of the colors developed.

Procedure

Total P_2O_5—Five grams of the sugar were mixed in a platinum dish with 0.2 gram of anhydrous sodium carbonate. The mixture was carefully charred over a free flame and finally incinerated to white ash in a muffle furnace heated to a temperature below that at which the ash will fuse. The ash was cooled, dissolved in exactly 1 cc. of nitric acid reagent, and taken up in a little hot water. The solution was filtered, and the filtrate and washings were collected in a 100-cc. Nessler tube and allowed to cool to room temperature. The reagents were then added in the same order and the same quantities as described for the standard tubes. After 30 minutes the solutions were compared colorimetrically with standards which had been developed at the same time.

Inorganic P_2O_5—Ten-gram portions of the sugars were dissolved in a little water in the Nessler tubes. To these solutions the reagents were added exactly as already described, and the colors which developed in 30 minutes were compared with those in the standard tubes.

Organic P_2O_5—The value found for inorganic P_2O_5 was subtracted from that found for total P_2O_5.

Table I gives the results found in representative white sugars.

Table I—Phosphorus as P_2O_5 in White Sugars

Sample	Inorganic P_2O_5	Organic P_2O_5	Sample	Inorganic P_2O_5	Organic P_2O_5
	P. p. m.	*P. p. m.*		*P. p. m.*	*P. p. m.*
Direct consumption beet sugars			Direct consumption cane sugars		
a	0.9	10.6	*p*	3.7	18.7
b	0.9	4.9	*q*	2.6	7.7
c	0.9	8.3	*r*	0.9	2.6
d	0.3	6.6	*s*	0.9	0.3
e	0.3	9.7	*t*	2.0	6.0
f	0.3	8.9	Refined cane sugars		
g	0.3	45.6			
h	0.3	5.4	*u*	0.0	4.9
i	0.3	11.3	*v*	0.0	9.2
j	0.3	8.9	*w*	0.0	6.3
k	0.9	4.9	*x*	0.6	6.9
l	0.9	8.3	*y*	0.0	6.9
m	0.6	2.9	*z*	0.0	0.6
n	0.9	7.2			
o	1.4	8.9			

In the determination of the total phosphorus it is essential to add sodium carbonate to the sugar before the charring in order to prevent the volatilization of some of the phosphorus pentoxide which will occur if there is not sufficient alkali or alkaline earth in the sugar to fix the phosphorus as phosphates in the ash. Table II shows the results obtained when the carbonate was added before incineration in comparison with those in which the carbonate was added after the incineration but before the treatment with nitric acid.

Table II—Effect of Time of Adding Carbonate on Total Phosphorus

Sample	Phosphorus as P_2O_5: Na_2CO_3 added before incineration	Phosphorus as P_2O_5: Na_2CO_3 added after incineration
	P. p. m.	*P. p. m.*
f	9.2	8.6
g	45.9	45.9
h	5.7	5.2
p	22.3	18.6

In dissolving the incinerated ash, the presence of some nitric acid is desirable to hasten the transformation of pyrophosphate to orthophosphate, since the latter is the only form of phosphorus which will react with the molybdate reagent. If an excess of nitric acid is used, however, it will interfere with the development of the color so that the results obtained will be too low. Thus, a determination of total phosphate in sugar *u* was made in which the ash was dissolved in 2 cc. of the dilute nitric acid and compared with one in which only 1 cc. was used. The former showed only 0.57 p. p. m. P_2O_5 while the latter showed 4.87 p. p. m.

A few of the colors developed from incinerated sugars had, in addition to the blue of the reduced molybdate, a slight yellowish cast caused probably by a small amount of iron in the ash of the sugar. It was found that the interference of this yellow color could be eliminated by viewing the unknown and the standard solutions with which it was being compared through a yellow Wratten light filter (K-3 No. 9), which equalized the colors and made possible a perfect match.

As in all colorimetric work, blank determinations should be made on the reagents without sugar and, if phosphates are found, suitable corrections must be made on the readings obtained with the unknowns.

The occurrence of such large proportions of organic phosphorus in refined sugars is unexpected. The explanation must be sought in further studies on the elimination of phosphorus during the refining processes.

Literature Cited

(1) Ambler, *Intern. Sugar J.*, **29**, 382, 437 (1927).
(2) Bell and Doisey, *J. Biol. Chem.*, **44**, 55 (1920).
(3) Briggs, *Ibid.*, **53**, 13 (1922).
(4) Rümpler, "Die Nichtzuckerstoffe der Rüben," pp. 32, 242, 302–21, and 352–5, Vieweg, Braunschweig, 1898.
(5) Shorey, *J. Am. Chem. Soc.*, **20**, 113 (1898); **21**, 609 (1899).
(6) Willstätter and Lüdecke, *Ber.*, **37**, 3755 (1904).

Flow Divider for Fractionation under Diminished Pressure[1]

A. M. Schwartz and M. T. Bush

Cornell University, Ithaca, N. Y.

ALTHOUGH a large amount of work has been done on the design of equipment for laboratory fractional distillation at ordinary pressures, relatively little attention has been paid to equipment for fractionation under diminished pressure. Most of the methods now in use provide for reflux, if at all, by means of partial condensation of the vapors. This is open to the serious objection that it is extremely difficult to control the reflux ratio. The alternate method of total condensation and the return of part of the condensate as reflux permits complete and easy control. This is especially necessary in vacuum fractionation as the vapor volumes are relatively large, and the efficient washing of this attenuated vapor in the column is not easy.

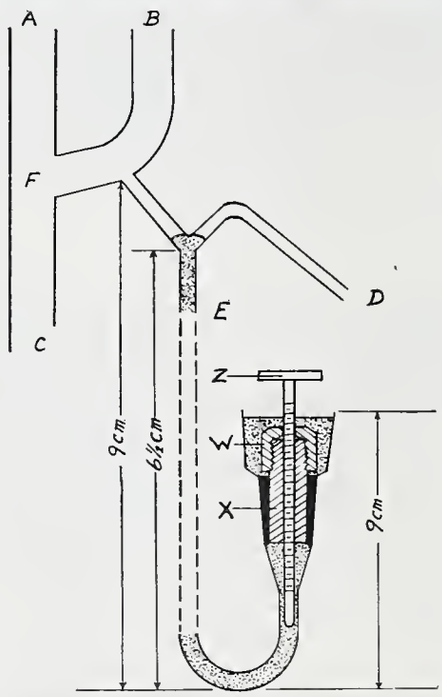


Figure 1—Stillhead and Mercury Valve

The ordinary method of providing a divided flow by means of a stopcock regulator is fairly satisfactory for ordinary pressures. In vacuum, however, it is open to several objections. The stopcock invariably freezes, especially if the temperature is above 100° C., there is contamination of the distillate by stopcock grease, and the regulation is not particularly delicate. The stillhead described, with a mercury check valve, has been found to be excellent, simple to make, and subject to none of the disadvantages listed above.

The upper part of the diagram, Figure 1, represents the stillhead itself, which is of ordinary design. *A* carries the thermometer, the bulb of which is placed at *F*. *B* carries a reflux condenser, and *C* fits into the column. The forward flow is through the bent tube *D*. At *E* the valve is sealed on, as indicated by the dotted line. The valve is shown relatively larger than its actual size, in order to bring out more clearly the details. The rate of flow is regulated by raising or lowering the level of the mercury in the elbow. This is accomplished by means of a steel plunger, *Z*, which screws into a hollow metal cylinder, *X*. This cylinder is threaded on the inside to fit the plunger, and also on the top part of the outside to fit a packing cap, *W*. It is cemented into a taper at the end of the Y-tube. A leather washer may be used as packing for *W*, which is necessary to prevent leakage. The plunger is lubricated with a generous supply of stopcock grease, and the whole assembly, with the exception of the upper part of the plunger, is submerged in a well of mercury as shown.

Owing to the inclusion of air in the threads, it is necessary to fill the device in a vacuum, as follows: The well at the top of the taper is made from a ground-glass joint. For the purpose of filling the valve, the male joint which fits the well is sealed to a stopcock. This is put in place and the apparatus evacuated through the delivery tube, *D*. The whole is inverted and mercury allowed to flow up through the stopcock to the bend in the U-tube. The stopcock is then closed and the vacuum released through *D*, which is then covered with a rubber nipple to prevent loss of mercury. The apparatus is now carefully turned upright while the stopcock is slowly opened to prevent air from entering the well. The excess mercury is allowed to run out and the male joint bearing the stopcock is removed. The packing box and plunger are put into place, the latter is screwed down tightly, and the height of the mercury in the elbow is adjusted. At this point the packing box is completely covered with mercury, which, for convenience, may be covered with a layer of paraffin.

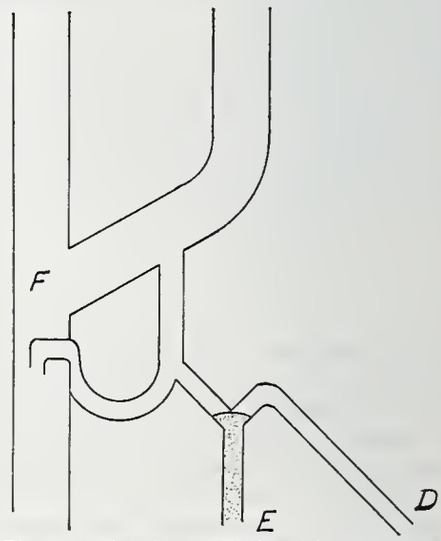


Figure 2—Modified Stillhead for Accurate Temperature Readings

The dimensions of the valve may vary within considerable limits. One of very convenient size is as follows: The outlet tube, *D*, is made of 4-mm. heavy-walled tubing, which increases the strength and lessens the holdup. The stem of the valve is of ordinary 6-mm. tubing, flared out at the top to a taper in which *X* sits snugly. The well is made from the lower half of a No. 2 female universal ground-glass joint, necessitating the use of pincers to screw down the packing cap. The external diameter of *X* is 6 mm., and with the packing cap it is 3 cm. over-all in length. The cap itself is 9 mm. long and has an external diameter of 8 mm. The plunger

[1] Received October 22, 1930.

is 9 cm. long and 3 mm. in diameter. The dimensions of the assembly are shown on the diagram.

The surface of the mercury at *E* may be cleaned readily by pouring in a suitable solvent and then expelling it through *D* by plugging up *A* and *C* and blowing at *B*. If the surface of the mercury is oxidized or corroded, a small portion of the mercury itself may be expelled in the same way. Thus it is only occasionally necessary to refill the divider. This device has proved to be satisfactory at pressures as low as 1 mm. The adjustment is sensitive, and the screw turns easily.

If the tube *A-C* is of small bore, say less than 15 mm., the reading of the thermometer may be affected by the proximity of the cold reflux returning from *B*. We may modify the construction of the stillhead itself so as to return the reflux at a lower point, as shown in Figure 2. This construction gives rigidly accurate temperature readings, but is fragile. A simpler, although not quite as effective method of eliminating thermometer error is to flare out the joint at *F* into a bulge of 2 to 3 cm. in diameter. The returning stream is then far enough away from the thermometer bulb not to affect the reading.

A simpler valve, one which may be used where there is not a large amount of fractionation to be continuously done, can be made from the same stillhead. At *E*, instead of sealing on the valve, a piece of rubber tubing is slipped over the stem. This is closed tightly at the far end, and is filled with mercury. The level of the mercury in the elbow is controlled by an ordinary pinchcock around the rubber tubing. This device is quite as efficacious as the more complicated one. Its disadvantage is that it is difficult to keep the tube from leaking over long periods of time.

Glass Temperature and Float Regulators[1]

D. F. Othmer[2]

Eastman Kodak Company, Rochester, N. Y.

The development of industrial processes on a laboratory and pilot-plant scale is frequently hindered by the lack of controlling apparatus of such simplicity and smallness as will fit in with the minute process equipment employed. Several types of temperature and float controllers representative of those which have been successfully employed are described as being suitable not only for use with ordinary chemical laboratory apparatus, but adaptable to the regulation of pilot-plant distillation and related operations.

LARGE distillation projects are usually developed as a result of studies made with small units, and in the operation of such pilot equipment it is frequently desirable to have apparatus to regulate the processes similar to the automatic controllers of industrial usage. The electrical thermostat circuit described (*3*) in a previous paper has been used as a pressure regulator for glass and pilot-plant stills and, by means of its use with an inclined manometer and an internal electric heater, a very constant rate of distillation may be maintained. A similar manometer circuit with the bulb of a vapor-pressure or liquid-expansion thermometer as the sensitive element may be used for controlling temperature, but it has the disadvantage of a simple on-and-off regulator with no intermediate steps automatically controlled.

A self-contained temperature controller using a vapor pressure bulb as the sensitive element and requiring no auxiliary power is shown in the accompanying figures.[3] Its use as applied to control of stillhead temperature by regulation of the amount of wash liquid returned to a fractionating column is indicated in Figure 1. The sensitive bulb of Figure 2 is inserted above the dephlegmator condenser of a double condenser unit (*2*) and maintains the temperature of the vapor stream between the two condensers at a constant predetermined value. It is previously charged with a liquid of suitable volatility, preferably one with a vapor pressure of about 90 to 125 cm. of mercury, at the temperature to be maintained. Only enough of the volatile liquid is required to give always a liquid phase. A bubble of air is allowed to remain to insure a gas and vapor phase, and the rest of the tube is filled with mercury. The bulb is readily charged by connecting with a straight glass cock, evacuating with a water pump, disconnecting the vacuum hose, and opening the cock with the free end under the liquid surface of a dish containing both the volatile liquid and mercury. The desired amount of volatile liquid is drawn in first, then mercury is allowed to fill the rest of the tube.

The flow controller, Figure 3, is mounted above the condensers and its bottom outlet connected to the inlet tube of the sensitive bulb. The connecting tube is filled with mercury and the system heated to the desired operating temperature, as shown by an auxiliary thermometer. The level of the flow controller is adjusted so that the vapor pressure of the liquid in the sensitive bulb at the set temperature forces the mercury high enough to submerge the inverted V-weir of the central tube.

Cooling water flows into the tube at the upper left of the flow controller and, when the mercury is below the level of the weir, down the annular space, up through the inner tube, and out through the discharge tube on the left to waste. As the mercury rises and throttles the flow through the weir, the water rises in the central tube and overflows the tube on the right side. Both outflow tubes have insealed tips to enable visual inspection of the comparative amounts flowing in each, and are vented to prevent siphoning. The right, and higher outlet discharges through a rubber tube to the base of the dephlegmator coils and furnishes cooling water for condensing the liquid to be refluxed as wash. As the temperature in the head of the dephlegmator rises, the flow of water through the weir and to waste is throttled and a larger amount overflows the right tube and thus passes through the dephlegmator condenser. This additional cooling water produces more condensate, which, by its washing action in the rectifying column, reduces the amount of high boilers in the vapor and therefore the temperature. Because of the lag caused by the small time interval in the change of the distillation with a change of reflux ratio, the amount of cooling water required is never exactly obtained as a steady stream, and the temperature varies slightly with accompanying changes in flow of cooling water

[1] Received November 3, 1930.

[2] Present address, 356 Clay Ave., Rochester, N. Y.

[3] All the glass apparatus described and pictured herein has been constructed of Pyrex glass by the Technical Glass Co., 42 Galusha St., Rochester, N. Y., which is also prepared to supply additional equipment of same type.

to the dephlegmator. A much smaller variation is obtained owing to the taper of the weir, however, than would be possible with a simple on-and-off valve.

During the progress of a discontinuous distillation, as the liquid in the still pot approaches exhaustion of the more volatile component, a larger amount of wash liquid is required, and the temperature and mercury level increase slightly to furnish additional water to the dephlegmator. If a sensitive liquid is chosen with a vapor pressure a little over 100 cm. at the temperature to be maintained, the rate of change of vapor pressure with temperature will be such that a few tenths of a degree rise of temperature raises the mercury a centimeter or more to shut off the flow through the weir completely. In the operation of continuous distillation processes, the use of this regulator has enabled the maintenance of a boiling point of distillate never more than two-tenths of a degree high over a period of weeks of operation, practically without attention and with large changes in rate and composition of feed and rate of distillation.

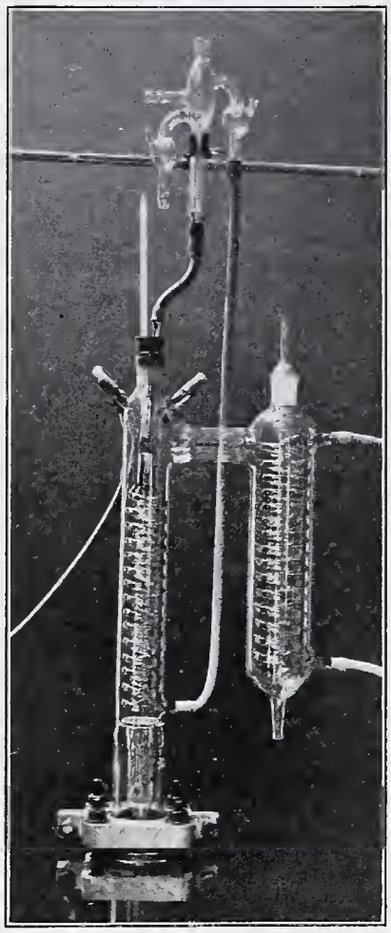


Figure 1—Temperature Controller Installed on Stillhead

The same regulation of larger pilot-plant distillation systems has been secured with this flow divider by using it to control the reflux ratio directly instead of controlling the water supply to a dephlegmator condenser. In this case, a single condenser is used for condensing all of the vapors and the sensitive bulb is mounted in the top of the rectifying column. The condensate flows through the flow divider directly, similar to the flow of cooling water in Figure 1, out through the left lower tube as product, and through the right connection as reflux to the column. The temperature at the head of the column and the resulting vapor pressure in the sensitive bulb control the mercury level in the flow divider which in turn regulates the ratio of product to reflux. A much larger amount of condensate may be handled in this manner, with a somewhat larger controller than that shown in Figure 3, and the time interval is reduced because of the comparative closeness of cause and effect.

This regulator has been adapted for numerous other uses in the regulation of pressure or temperature when a flowing liquid causes the change of conditions. It has proved an especially simple and efficient thermostat in water baths varying in size up to hundreds of liters. (For pressure regulation, the vessel with controlled pressure is connected to one arm of a U-tube filled with mercury, and the other arm is connected directly to the bottom outlet of the controller.) For holding temperatures between that of the room and that of tap water, at approximately 20° C., the regulator is used exactly as described above for controlling distillation processes. The sensitive liquid used is Eastman ethylene oxide, which has a boiling point of 14° C. and a suitable vapor pressure at 20° C. The vapor-pressure bulb is immersed in the bath and cold water from the right outlet runs directly into the stirred water, that from the left outlet runs to waste. An overflow pipe or siphon maintains a constant water level in the bath by allowing an amount equal to the cold water introduced to be discharged. An efficient stirring, accomplished by bubbling several jets of air through the water, must be maintained, as with any constant-temperature bath.

Figure 2—Vapor-Pressure Bulb

A control with reverse action to that described is made by simply interchanging connections on the left and right side arms. For temperatures above that of the room, any point below that of the hot water available may be maintained with one so arranged. The temperature of a 100-liter water bath was maintained at 40° C. within very narrow limits over a period of weeks with ethyl ether as a sensitive liquid, and hot water discharging through the left arm to supply the heat required. The hot water supply varied in temperature between 48° and 95° C. during different times of the day, but this variation merely changed the size of the stream necessary to supply the required amount of heat.

Baths with temperatures between 15° and 25° C. require provisions for both heating and cooling if the temperature of the room fluctuates widely from day to night or month to month. Such regulation may be accomplished with mercury or other metallic expansion systems, relays operating electrical heaters, and solenoid valves controlling cooling water circulated through coils of tubing. Besides the involved mechanism, and the simple on-and-off features in both heating and cooling devices instead of gradual increments of heat added or removed, these devices have the additional disadvantages of large expense and considerable space requirements in a bath. The utilization of two liquid flow controllers, one diverting a stream of cold water and the other reversed in action and diverting a stream of hot water, accomplishes the same purpose with a single sensitive bulb in the bath connected to the two flow controllers.

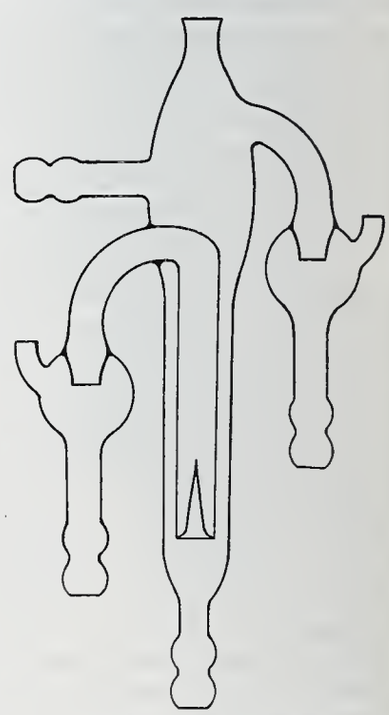


Figure 3—Flow Diverters

Figure 4 pictures such a system ready for mounting in the bath but with the bulb indicated as if heated to force the mercury into the divider. The flow controller on the left is "direct acting" for cold water, that on the right is "reverse acting" for hot water. The extra length of the sensitive bulb is a precaution to prevent the very volatile liquid from blowing out the mercury in case it is allowed to come to room temperature. The vapor pressure of ethylene oxide at room temperature is less than the height of mercury in the inner tube when the mercury is forced down and practically out of the annular space by the vapor pres-

Figure 4—Combined Hot- and Cold-Flow Controllers for Heating and Cooling

Figure 5—Double-Flow Controller for Heating and Cooling

sure. The feed connections are as before, the left to cold, the right to hot water. The two inner outflow connections go to waste and the two outer connections go to the bath. The two weirs are at the same height and the increase of vapor pressure in the bulb raises the mercury level to throttle both simultaneously. This increases the cold-water flow and decreases the hot-water flow to the bath, the respective flows to waste changing to compensate.

A combination of two of these regulators with mercury, waste, and bath connections joined is shown in Figure 5. The comparative compactness and simplicity of the connections is apparent and this type may be set up very readily. A small adjustment of relative heights of weirs to change the flow of the hot and cold water with respect to each other may be made if desirable by tilting the apparatus to throw either side slightly higher. Thus it is possible to stop the flow of cold water to the bath at one temperature and start the flow of hot water at another temperature, lower by 0.05° C., say. Usually, however, the weirs are at exactly the same height and the streams of both hot and cold water are throttled so that a mixture of the two streams is discharged to the bath at just the average temperature required to equalize the amount of heat flowing into or out of the bath due to other causes. The same arrangement would obviously serve to supply a stream of liquid of any desired temperature by mixing a hot and a cold stream.

A large gas-heated feeding tank has been maintained at a temperature constant within 0.2° C. by controlling the gas fed to the burner with a regulator such as shown in Figure 3. Gas is introduced through the upper left side arm and discharged through the lower left side arm, all other openings save the bottom being plugged. Mercury, actuated by a vapor pressure bulb, is used to throttle the flow of gas. A pilot light is, of course, necessary to relight an extinguished flame.

The same type of vapor-pressure bulb that actuates all of the above-mentioned flow diverters has been used to open and close valves or cocks where a closed system under vacuum or pressure must be regulated. Figure 6 shows a typical member of this series. It is simply an ordinary cock having a short glass tube for a handle through which is placed a beam terminating in two mercury reservoirs. The left arm is connected to a sensitive bulb which, on increase of temperature, forces mercury into the reservoir. This counterbalances the mercury placed as a weight in the right reservoir, gradually overbalances it, and rotates the plug within the seat to open or close the valve, depending on the relative position of the bore in the plug and barrel. The desired leverage and travel is adjusted by varying the position of the cock along the beam and adding mercury to the reservoir on the right.

Such a force or weight, variable with changes of temperature or pressure, may be applied to other uses, such as raising a piston, globe, or gate of a small metal valve, or pinching a light-walled rubber tubing to constrict or stop the flow. In any case the vertical motion downward is usually comparatively rapid, since the lowering of the upper mercury level causes a rapid flow of mercury to balance the vapor pressure, and the cause and effect are cumulative until the movement is mechanically checked or until the system as a whole comes to the equilibrium or steady state desired. A mechanical advantage by fluid balance, similar to that which has been utilized for sensitive manometers (*1*), gives a great increase of power to such mechanisms.

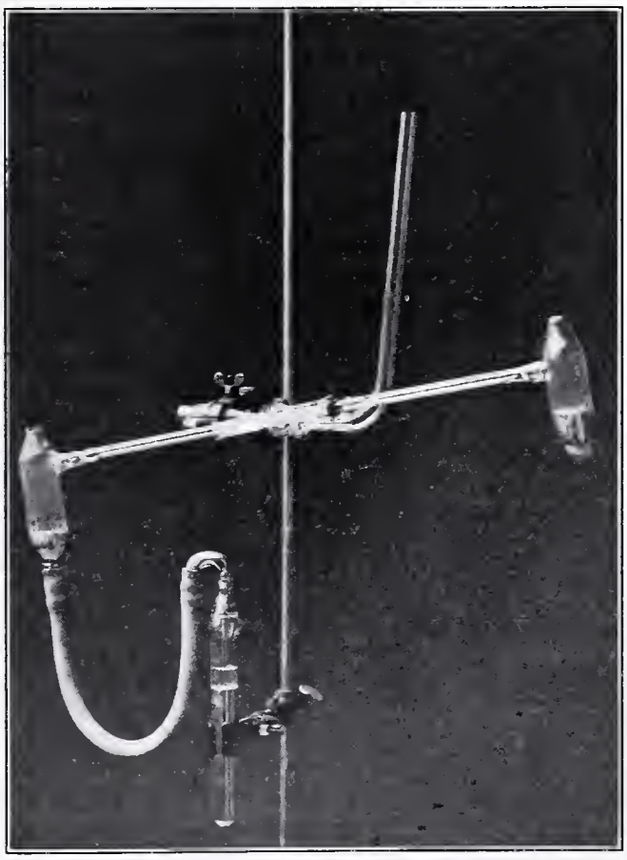


Figure 6—Mercury-Weighted Cock

Float Controls

For maintaining a constant liquid level in various small vessels, baths, feeding bottles or siphons, and still pots, several types of float valves constructed of glass have been used. The first of these, Figure 7, allows liquid to flow through the upper inlet tube into the container until the ball float rises

and the rubber valve seat throttles or closes the mouth of the inlet tube. The neck of a 200-cc. Pyrex spherical flask is removed and a stem of 8-mm. glass tubing sealed on in its place. The top closed end of this stem is capped with a piece cut from a rubber stopper of suitable size. This rubber cap and valve seat is notched on the lower side to allow liquid to

Figure 7—Inflow Float Valve with Rubber Seat

Figure 8—Outflow Float Valve, Intermittent Type

flow around it and down to the container beneath. The outer tube is of suitable size to act as a bearing for the vertical motion of the stem, and is enlarged at the top to accommodate a rubber stopper holding the inlet tube. The device as illustrated is for use in Pyrex 22-liter flasks, may be inserted through the 75-mm. neck, and is firmly supported in a hole in the rubber stopper. The level desired is regulated either by changing the length of the stem or by sliding the whole unit to the desired position in the rubber stopper. Such a level regulator has been used over a period of weeks at a time to control the level of acetone boiling in a flask, and it allowed acetone from an overhead storage tank to flow into the still pot to replace that distilled out through a system of rectifying columns. The level of the boiling liquid did not change perceptibly while the float was in operation, and when it was desired to shut down overnight or for other reasons, no attention was required, as this valve closed tightly.

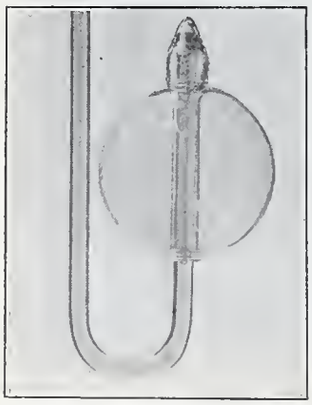


Figure 9—Outflow Float Valve, Constant-Level Type

In the operation of continuous distillation operations, it is usually desirable to allow the slops, higher boiling residue, or product to flow out from the base heater. A type of float control which may be used for this overflow service as well as the inflow service of the one described above, is pictured in Figure 8. In this valve the stem is separate from the float and is enlarged to form a hollow plug pierced by several holes as shown. A tube is sealed through the float of a size suitable to act as a bearing for the stem and is enlarged to form the sleeve for the plug. The sleeve and plug are ground to a good joint, and a small hole to equalize the pressure above and below the ground joint is blown between it and the float bulb.

When used to drain a vessel to a minimum level, this regulator is set in the position illustrated, and the lower end of the stem is sealed off or stoppered. The upper end is supported rigidly and connected to a suitable siphon which draws liquid between the ground surfaces, through the holes in the hollow plug, and up through the stem when the float is raised. As the liquid level lowers, the sleeve of the ground joint seats itself on the plug to close the perforations, and the liquid stops flowing. This valve works intermittently and dumps the liquid between a high level necessary to cause the ground joint to unseat, and a low level at which a tight joint is again made. It is useful as a feeder for glass-packed columns for distillation or gas-absorption systems where an intermittent-flooding feed is desirable. In such service it has worked unattended for hundreds of consecutive hours.

Figure 10—Steam or Vapor Trap of Float Type

The float control of Figure 8 is also used for regulating the inflow of liquid to maintain a constant level when the rubber seat of the one in Figure 7 is undesirable. It is then inverted from the pictured position and the end of the stem opposite the ground plug is sealed off. Liquid flows through the stem and the perforations in the plug when the float is down, and the stream is cut off as the float rises. In this position this valve throttles and the liquid level is maintained within very narrow limits.

Still another type which is all glass and is able to work against a higher pressure difference than the one of Figure 8 is shown in Figure 9. The liquid flows up through the annular space past the ground seat and out the exit tube. A very short, blunt tip on the inner tube is ground into the seat and, because of the very small amount of friction and the minimized chance of seizing owing to the bluntness of the ground joint, this valve maintains a constant level against a discharging flow. It will maintain a level practically constant within a flask boiling with an internal pressure up to several pounds per square inch by discharging accumulated residue to atmospheric pressure. It is equally useful for maintaining a constant level in feeding tanks and other similar vessels, or when inverted it acts as a throttling inflow valve. Its small ground surface, compared with that of the one in Figure 8, makes it a more sensitive and powerful valve.

The glass float of Figure 10 serves in the pictured position as a steam or vapor trap. It has served several purposes where a separator for liquids and vapors was desired, and is particularly useful for discharging liquid from a glass still pot. The liquid flows through the upper cock and fills the float chamber until the buoyancy on the float causes it to rise, unseat the ground glass joint at the bottom, and discharge, without breaking the seal, a part of the accumulated liquid. The side arm near the bottom serves to drain the float or by-pass the liquid, and the glass points on the float keep it free from the inner walls of the chamber. A pressure differential up to five pounds per square inch across the trap shown has been used but, for higher pressure differences, a bulb with a larger volume and buoyancy or smaller ground exit would be required. In an inverted position this device when connected to a source of supply of liquid may be used to maintain a constant head on the cock, and hence a constant flow. Rise of liquid in the chamber above the buoyant level raises the plug and stops the flow, and the opposite condition brings

about the opposite effect. In this service, unless only very small differences of pressure of the liquid supply are to be smoothed out, the control is no better than that of a Marriott bottle.

Literature Cited

(1) Hickman, *J. Optical Soc. Am.*, **18**, 305 (1929).
(2) Othmer, Ind. Eng. Chem., **22**, 322 (1930).
(3) Othmer, *Ibid.*, Anal. Ed., **1**, 97 (1929).

Comparative Efficiencies of Gas-Washing Bottles[1]

F. H. Rhodes and D. R. Rakestraw

Cornell University, Ithaca, N. Y.

The investigation described in this article was undertaken for the purpose of obtaining information as to the comparative efficiencies of some of the types of gas-washing bottles commonly used in chemical laboratories. Each test was made by passing a known mixture of air and carbon dioxide through a solution of sodium hydroxide contained in the bottle, and determining the percentage of carbon dioxide in the exit gas at various rates of flow.

The apparatus used is shown in Figure 1. Carbon dioxide from a cylinder of the liquefied gas was passed through a capillary orifice meter, *A*, and mixed with air which was admitted through a second orifice meter, *B*. By maintaining a constant reading on each of the two manometers, A_1 and B_1, mixed gas of constant composition was obtained.

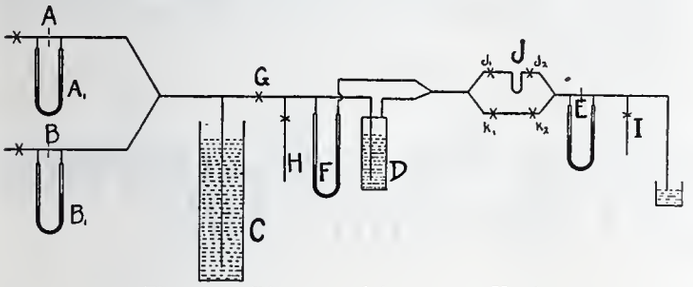


Figure 1—Diagram of Apparatus Used

Constant pressure on the discharge side of the orifice meters was maintained by keeping the rate of flow of gas high enough to maintain constant flow of gas through the water-sealed discharge tube, *C*. The mixed gas was passed through a solution of sodium hydroxide in the bottle to be tested, *D*, and then through a calibrated orifice meter, *E*, which measured the rate of flow of the exit gas. A manometer, *F*, was connected across the line so as to measure the drop in pressure through the bottle. The rate of flow of gas through the train was regulated by the stopcock *G*. Samples of the inlet gas were collected at *H;* the outlet gas was sampled at *I*. A by-pass was placed in the exit-gas line so that the washed gas could be passed through a U-tube, *J*, containing a solution of barium hydroxide. Samples of gas for analysis were collected in a Hempel buret over mercury and were analyzed by absorbing the carbon dioxide in a solution of caustic soda contained in a Hempel pipet.

The bottle to be tested was filled to the normal working height with a solution of sodium hydroxide (32.7 grams per liter) and was inserted in the train. Air was passed through the system to sweep out any carbon dioxide that might be present. A clear solution of barium hydroxide was placed in the U-tube, *J*, and stopcocks J_1, J_2, K_1, and K_2 were set so that all of the exit gas passed through this solution. If no precipitate appeared within 3 minutes, the current of air was discontinued and a mixture of air with a known amount of carbon dioxide was passed very slowly through the system. If no precipitate appeared in the U-tube within 3 minutes, the rate of flow of the gas was increased slightly and an observation was taken as before. Repeated tests were made at increasing rates of flow until a point was found at which the carbon dioxide in the inlet air was no longer completely absorbed by the alkaline solution in the wash bottle.

After the point at which complete absorption can be obtained was determined, the stopcocks in the discharge line were set so that all of the gas passed directly to the orifice meter, *E*, and tests were made at higher rates of flow. At each rate, observations were taken to determine the rate of flow of the exit gas, the percentage of carbon dioxide in the exit gas, and the drop in pressure through the washing bottle.

The gas-washing bottles tested were as follows:

Bottle	Type	Height of Soln. during Normal Operation
		Cm.
1	Muencke	10.5
2	Friedrichs spiral	11
3	Habermann	11
4	Habermann	14.5
5	Schott and Gen. (Jena), with sintered-glass distributing plate, inlet tube at center of plate	12
6	Schott and Gen., with sintered-glass distributing plate, inlet tube at side of plate, pattern No. 83	12
7	Schott and Gen., sintered-glass distributing plate, pattern No. 101	15.5
8	Muencke, with space between inlet tube and wall of bottle filled with glass beads approx. 3 mm. in diameter	10.5

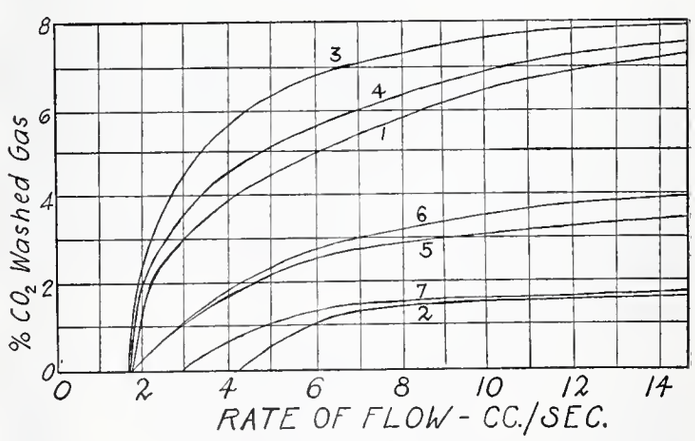


Figure 2—Determination with 13.4 Per Cent CO_2 in Inlet Gas

Two series of determinations were made, one with an inlet gas containing 13.4 per cent of carbon dioxide, and the other with an inlet gas containing 5.1 per cent of carbon dioxide. The results are shown in Figures 2 and 3.

The tests made with the inlet gas of high concentration show that the Friedrichs spiral gas-washing bottle was the most efficient of all the forms tested by us. No carbon dioxide could be detected in the exit gas until the rate of flow exceeded 4.3 cc. per second, and even at higher rates the percentage of unabsorbed carbon dioxide in the outlet gas was

[1] Received December 10, 1930.

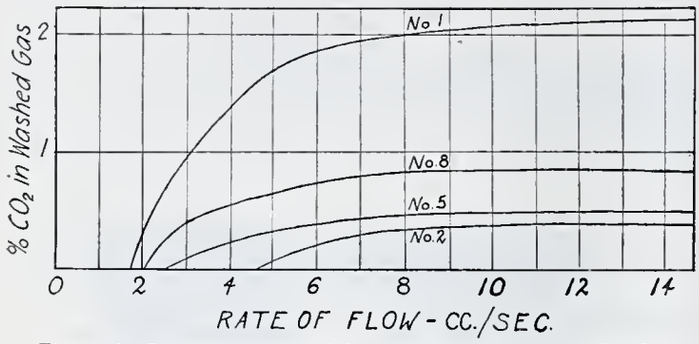


Figure 3—Determination with 5.1 Per Cent CO_2 in Inlet Gas

low. Bottle 7 (Schott and Gen. pattern 101) gave results only slightly inferior to those obtained with the bottle of the spiral type. The poorest results were obtained with the bottles of the Muencke and the Habermann types, the Muencke bottle being only slightly more efficient than the Habermann bottles. Somewhat similar results were obtained in the experiments made with the inlet gas that contained only 5.1 per cent of carbon dioxide. Decreasing the concentration of the absorbable component in the original mixture has comparatively little effect in increasing the maximum rate at which the gas can be passed through any particular bottle without allowing a detectable amount of carbon dioxide to pass through unabsorbed. A comparison of curves 1 and 8 in Figure 3 shows that the efficiency of the commonly used Muencke bottle can be increased to a considerable extent by filling the space between the inlet tube and the wall of the bottle with glass beads.

From the results shown in Figure 4 it is apparent that

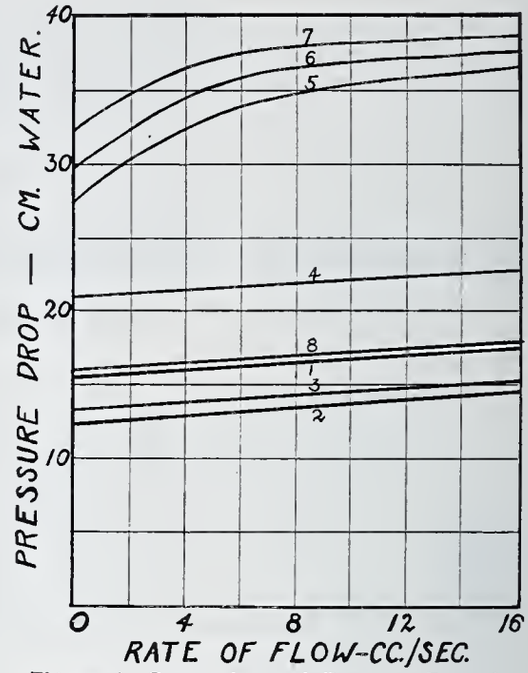


Figure 4—Comparison of Pressure Drop in Various Bottles

the drop in pressure is considerably greater in those bottles that are provided with a distributing plate of sintered glass. This is to be expected, since in bottles of this type pressure is required not only to overcome the static head of the liquid, but also to force the gas through the small pores of the distributing plate.

Alignment Chart for Estimating Viscosity-Gravity Constant of Petroleum Lubricating Oils[1]

W. F. Houghton and J. A. Robb

The Atlantic Refining Company, Philadelphia, Pa.

THE viscosity-gravity constant as developed by Hill and Coats (*1*) has been found to be a great aid in defining and classifying lubricating oils. It affords a convenient means for following the progress of various refining processes such as acid treatment and solvent extraction. From tests on the heavier fractions of crude oils, it gives an excellent clue to the properties of all the fractions. Table I gives the viscosity-gravity constants of lubricating cuts from various crude oils and shows the value of this index as a means of classification and identification.

Table I—Viscosity-Gravity Constants of Lubricating Cuts from Various Crude Oils

Sour Lake, Tex.	0.916	Reagan County, Tex.	0.839
Heavy Mexican	0.894	Salt Creek, Wyo.	0.829
Sunset, Calif.	0.885	Burbank, Okla.	0.828
Spindletop, Tex.	0.876	Ranger, Tex.	0.827
Light Mexican	0.860	Eureka, Pa.	0.804
Van Zandt County, Tex.	0.852	Buckeye, Ohio	0.800
Seminole, Okla.	0.844	Milltown, Pa.	0.800

The viscosity-gravity constant is based on a relation between Saybolt viscosity and specific gravity as follows:

$$G = A + \frac{1.0752 - A}{10} \log (V - 38)$$

where A = viscosity-gravity constant
G = specific gravity at 60° F. (15.6° C.)
V = Saybolt viscosity at 100° F. (37.8° C.)

When the viscosity is measured at 210° F. (98.9° C.), the following equation is used:

$$G = 0.24 + 0.755A + 0.022 \log (V' - 35.5)$$

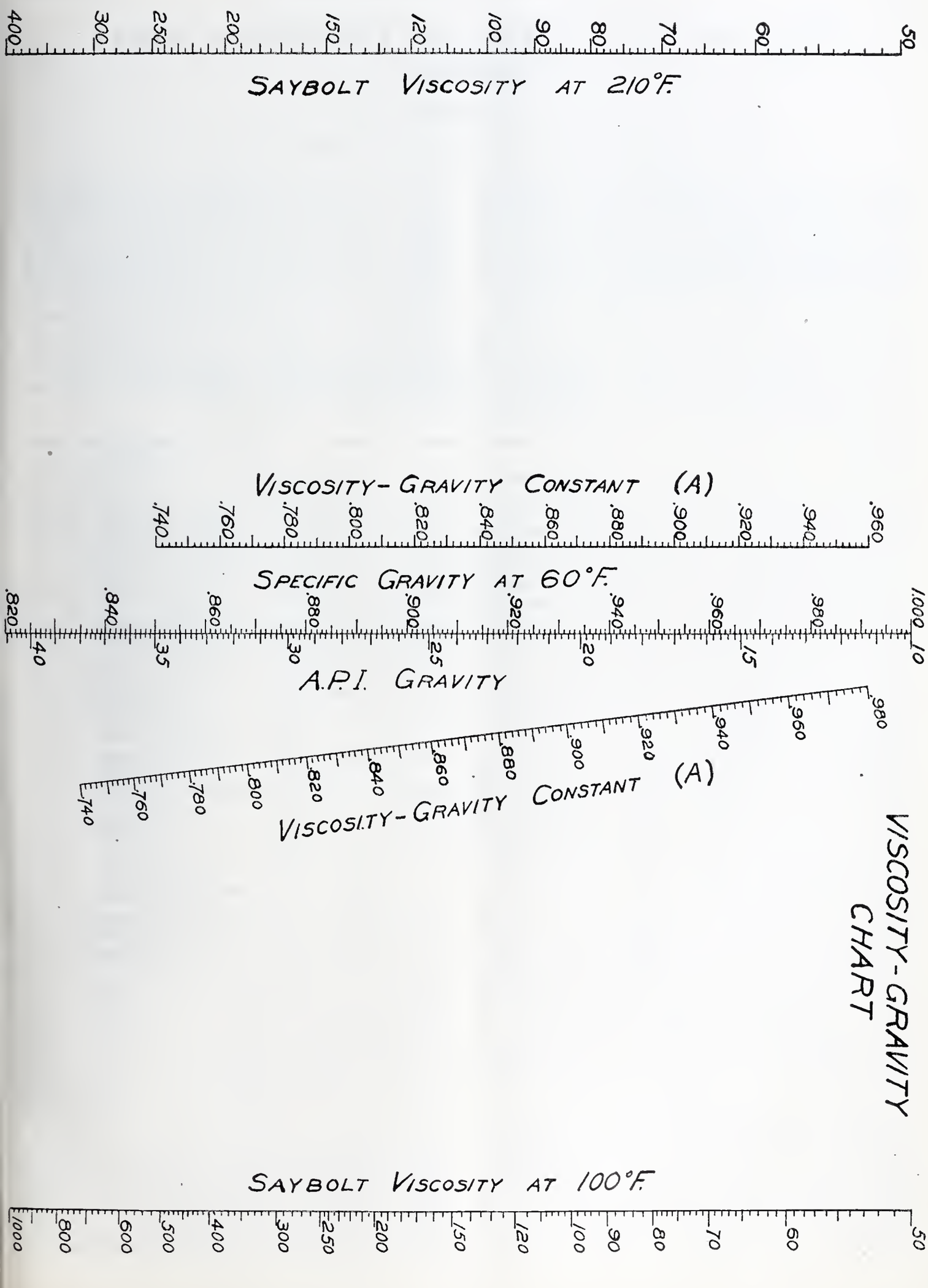
where V' = Saybolt viscosity at 210° F. (98.9° C.)

These equations are rather cumbersome and make the calculation of the constant so tedious as to detract from its general usefulness. To eliminate this factor, an alignment chart has been constructed which permits the rapid estimation of the constant from the viscosity and gravity data. In this chart the left side is to be used for viscosities at 210° F. (98.9° C.) and the right side for viscosities at 100° F. (37.8° C.). In using the chart for the evaluation of A, connect by means of a straight edge the proper mark on the viscosity scale with the corresponding value on the gravity scale. Then the value of A is given by the intersection of this line with the viscosity-gravity constant scale. For example, a Winkler distillate has a viscosity of 92 Saybolt seconds at 210° F. (98.9° C.) and a gravity of 18.6° A. P. I. The constant is found to be 0.880. Another distillate has a viscosity of 350 Saybolt seconds at 100° F. (37.8° C.) and a gravity of 28.4° A. P. I. The constant in this case is 0.822. This distillate falls in the class of highly paraffinic mixed-base lubricating crudes such as Williamson County, Texas.

[1] Received November 7, 1930.

Literature Cited

(1) Hill and Coats, Ind. Eng. Chem., **20**, 641 (1928).



VISCOSITY-GRAVITY CHART

Determination of Barium Fluosilicate Spray Residue[1]

R. H. Carter

Insecticide Division, Bureau of Chemistry and Soils, Department of Agriculture, Washington, D. C.

THE introduction of substitutes for arsenical compounds in the control of insect pests brings up the question of the determination of the amount of residue left on food products. Determination of the amounts of such compounds applied by different methods of spraying and dusting is also important from the standpoint of ascertaining the efficiency of the compounds and their weathering qualities.

In the Pacific Northwest barium fluosilicate was given extensive tests for the control of codling moth by E. J. Newcomer, of the United States Bureau of Entomology. The material used in these experiments was a commercial product containing about 80 per cent barium fluosilicate and 20 per cent fluffing agent. As there was no standard procedure for determining residues of barium fluosilicate it was necessary to devise one that was fairly rapid and as accurate as possible.

There are, of course, four possible ways for determining the quantity of such a compound—i. e., analyses for (1) barium, (2) silica, (3) fluorine, and titration with standard alkali. The determination of silica under such conditions is entirely unsatisfactory. Commercial barium fluosilicate contains varying amounts of hydrated and partially hydrated silica, and a special light form of barium fluosilicate contains precipitated silica as a diluent. In addition, considerable dust accumulates on fruit and foliage by the end of the season owing to the absence of rain so that determinations of silica are impossible. The determination of fluorine in small amounts is possible by several different methods, but none are entirely satisfactory. Some of the common methods give results which are consistently too low, while others are too cumbersome and involved for use under these conditions. Titration of the barium fluosilicate with standard alkali is not practical owing to the impossibility of its removal as such from the fruit. The determination of barium under standard conditions is accurate and reliable, and as there was no danger of errors due to added barium from the fruit or foliage this was decided upon as the best of the four methods.

There are two general methods for obtaining spray residue from fruit for analytical determinations: peeling and subsequent ashing or digestion of the peelings to destroy the organic matter, and washing with some solvent and analysis of the solution. The washing method, which is in common use for removal of arsenical residue, is much the more rapid and sufficiently accurate, so it was adopted. Because of its reaction with barium fluosilicate according to the equation

$$BaSiF_6 + 4NaOH \longrightarrow BaF_2 + 4NaF + Si(OH)_4$$

a dilute solution of sodium hydroxide was decided upon as being a satisfactory solvent, and the following procedure was developed.

Procedure

Samples of twenty apples of approximately uniform size were selected for analysis and the weight determined within 5 grams. They were then washed individually by immersion for approximately 30 seconds in a boiling 3 per cent sodium hydroxide solution and rinsed with slightly acidulated water. The combined rinsings and washing solution, totaling 400 or 500 cc., was then cooled, made strongly acid with hydrochloric acid, and filtered as rapidly as possible through filter paper. This filtration removed solid organic matter, etc., extracted from the apples during the washing process, and the filtrate was free of suspended matter but highly colored. The filtrate was made strongly alkaline with sodium hydroxide, then neutralized with sulfuric acid, and about 5 cc. in excess added to precipitate the barium as barium sulfate. The solution was boiled, cooled slowly, and allowed to stand 12 hours or longer. It was filtered through filter paper, the paper was washed, dried, and ignited in a muffle for 1 hour, and the ash weighed as barium sulfate, and then calculated to barium fluosilicate.

Table I—Determinations of Barium Fluosilicate Spray Residue

	Barium Fluosilicate *Grain/lb.*	Average *Grain/lb.*
Check (3 lbs. per 100 gal. in 5 cover sprays)	0.119 0.126	0.122
Check (4 lbs. per 100 gal. in 4 cover sprays)	0.129 0.129	0.129
Check (4 lbs. per 100 gal. in 5 cover sprays)	0.145 0.144	0.144
Washed with 0.5 per cent NaOH	0.028 0.034	0.031
Washed with commercial alkaline compound (60 lbs. per 100 gal.)	0.025 0.052	0.038
Washed with commercial alkaline compound (40 lbs. per 100 gal.)	0.041 0.067	0.054
Washed with 0.66 per ceut HCl	0.082 0.077	0.080
Washed with 0.66 per cent HCl + kerosene emulsion	0.086 0.085	0.085
Washed with 0.33 per cent HCl	0.090 0.117	0.103
Washed with 0.33 per cent HCl + kerosene emulsion	0.087 0.115	0.101
Wiped by hand	0.041 0.049	0.045
Washed with 0.5 per cent NaOH	0.031 0.023	0.027
Washed with 0.5 per cent NaOH soln. after 1 hour's use	0.031 0.046	0.038
Washed with 0.5 per cent NaOH soln. after 2 hours' use	0.058 0.050	0.054
Washed with 0.5 per cent NaOH soln. after 3 hours' use	0.039 0.031	0.035
Washed with 0.5 per cent NaOH soln. after 4 hours' use	0.040 0.042	0.041
$BaSiF_6$ (4 lbs. per 100 gal.)	0.109 0.124	0.116
$BaSiF_6$ (4 lbs. per 100 gal. + 0.5 pint fish oil)	0.116 0.118	0.117
$BaSiF_6$ (4 lbs. per 100 gal. + 1 pint fish oil)	0.112 0.128	0.119
$BaSiF_6$ (4 lbs. per 100 gal. + 2 pints fish oil)	0.115	0.115

Although this method may be subject to some criticism, it was fairly rapid and gave results that were consistent and capable of duplication. The data in Table I, giving duplicate analyses on a number of samples, indicate its reliability and consistency. The results are calculated in grains of barium fluosilicate per pound of fruit in order that comparison may

[1] Received December 1, 1930.

be made with results on arsenical residue determinations. It should be remembered, however, in making such comparison that these results express approximately 80 per cent of the total residue, whereas arsenical residue results are always expressed in grains arsenic trioxide per pound, which in the case of lead arsenate is probably approximately 30 per cent of the total residue. One point to be remembered in following this procedure is that the volume of solution must be sufficiently large at all times to keep in solution all barium fluoride and barium fluosilicate that may be formed before the final precipitation of barium as barium sulfate.

As shown in the table, these analyses were made on samples which had been subjected to considerably different treatments, including check samples which had received as many as five cover sprays, samples from the orchard immediately after spraying, and samples from commercial washing experiments with a number of different solvents on apples which had received five cover sprays of barium fluosilicate. Naturally, under such conditions considerable variation in duplicates may be expected, owing to variations in sampling. Actually, however, the agreement between the duplicate analyses was very close in most cases. The difference between duplicates which does not appear to be a function of the amount of residue, has a mean value of 0.011 grain per pound under the conditions of these experiments. This corresponds to an average error in the mean of duplicate determinations of ±7 per cent when the total residue approximates 0.08 grain per pound. This is probably within the limits of experimental error in sampling. Based on these results this method may be considered sufficiently accurate and reliable to give at least comparative results for the determination of barium fluosilicate as spray residue on apples.

Further Applications of the Centrifugal Filtration Tube[1]

Evald L. Skau and Louis F. Rowe

JARVIS CHEMICAL LABORATORY, TRINITY COLLEGE, HARTFORD, CONN.

Experimental data here reported show that the centrifugal filtration tube may be used satisfactorily for the approximate estimation of solubilities at different temperatures. The binary freezing-point diagram of the system benzene-naphthalene, which has been constructed by means of this method, shows fair agreement with the accurate diagram.

In such cases, as well as in water solutions of solids, the eutectic composition may be estimated by a single determination by means of this device. This is proved by experimental results for the above system and for the systems water–sodium nitrate and water–potassium iodide.

The centrifugal filtration tube should be applicable in any plant-control work in which, for example, it is desired to carry a reaction to a stage where a certain consistency or freezing point is reached. Instead of a rough determination of the freezing point, a determination of the amount of solid separated at some arbitrary temperature could readily be made with suitable accuracy.

THE centrifugal filtration tube, a simple contrivance for the rapid separation of solids from liquids at any desired temperature, has been described in a previous publication (*2*) and experimental data were there presented to show its usefulness in purification by recrystallization, especially in the case of compounds which require low-temperature technic for their separation.[2] The additional applications of this device are based upon the fact that it can be used to determine the approximate proportions of solid and liquid in a mixture at any definite temperature. It can therefore be used in certain cases for the rough construction of binary freezing-point diagrams and for the rapid estimation of eutectic compositions and temperatures, and has practical applications in plant control work.

Rough Construction of a Binary Freezing-Point Diagram

Instead of determining the freezing point of a given composition, the composition of the mixture having a given freezing point is found—that is, a mixture of known composition is brought to equilibrium at the desired temperature (below its primary freezing point) and the proportion of solid and liquid determined. The composition of the liquid can then be calculated.

A circular piece of filter paper about 1.5 cm. larger in diameter than the perforated porcelain disk C (Figure 1) is folded along a diameter and then slit with a pair of scissors part way across the perpendicular diameter starting at the center. The wire E is passed through this slit and the paper is pressed flat on the disk and folded well down over the edges. The disk is then pushed down upon the shoulder B so as to fit snugly to the walls of the tube.

The mixture of known composition is now weighed into the tube H, tube G is weighed and fitted into place, and the sample is melted completely by heating. The whole tube is then immersed for from 20 to 30 minutes in a thermostat set at the desired temperature, t, being protected from contact with the liquid of the bath.

Note—For temperatures above 0° C. a rubber sac such as may be made by cutting off the end of a toy balloon is suitable. For low temperatures where rubber cannot be used, the tube may be inserted within another glass tube.

It is then inverted quickly and immediately centrifuged for a few minutes. The liquid is thus thrown into chamber G, the bulk of the separation being accomplished within 20 seconds of the time when the tube was removed from the bath—that is, before the temperature has changed appreciably. The solid phase is now removed with the disk and the weight of the liquid in G ascertained. The solid phase must be identified.

Since this liquid was at equilibrium with the solid phase at the temperature of the thermostat, its freezing point is t. If the original mixture consisted of a grams of A and b grams of B, and if s_b grams of solid B have been separated out by centrifuging, the liquid having the freezing point t has the composition

$$\frac{a}{a+b-s_b} \text{ of } A \text{ and } \frac{b-s_b}{a+b-s_b} \text{ of } B$$

The mother liquor and the crystals may now be recombined and another determination may be made at other tempera-

[1] Received October 23, 1930.

[2] These tubes are now obtainable from Eimer and Amend, New York.

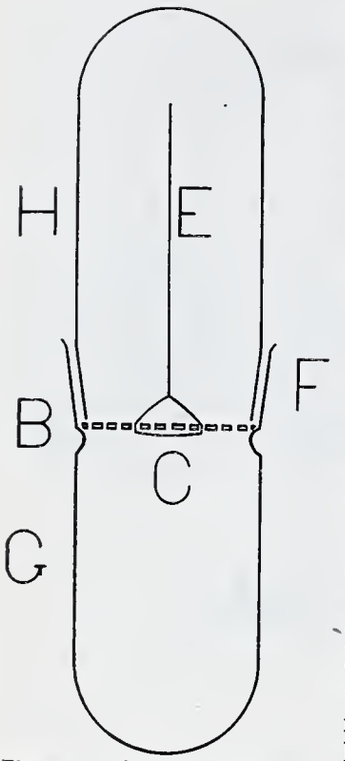


Figure 1—Centrifugal Filtration Tube (Inverted)

tures on the same sample if desired. It is recommended, however, that a fresh sample be used for each determination. In this way the whole freezing-point diagram of the system may be constructed, the freezing points of the pure constituents being obtained by one of the usual methods.

Eutectic Composition Found in One Determination

If the eutectic temperature were known the eutectic composition could easily be found by the above method. If, however, the eutectic temperature is unknown but lies below room temperature, the eutectic composition can be found by a single determination, provided one of the pure constituents is a solid at room temperature, by cooling a known mixture having an excess of that constituent to well below the eutectic temperature, thus solidifying the mixture completely in H, and then centrifuging it in the inverted tube while it is warming up so that any liquid is whirled off through the disk as soon as it is formed. Under these conditions the liquid collected in G will have the eutectic composition, and from its weight its composition can be calculated as above.

Let us consider, for example, the simple eutectic system benzene-naphthalene. If an equimolecular mixture (having a primary freezing point of 58.8° C.) be cooled to −20° or −40° C. and then allowed to come slowly to room temperature, liquid having the eutectic composition would start to appear at the eutectic temperature (−3.5° C.) and would continue to form at the expense of the two solids, the temperature remaining constant, until all of the solid benzene was used up. The excess of naphthalene would then start to dissolve in the eutectic liquid and the temperature would start to rise again until at room temperature, t° C., the mixture would consist of solid naphthalene suspended in a liquid whose freezing point is t° C. If this warming-up process took place during centrifuging as described above, however, the liquid formed at the eutectic temperature would be removed at that temperature before it had dissolved any more naphthalene, and the excess of naphthalene present at that temperature would be left on the disk, since its melting point is 80° C. Thus the amount of liquid and solid obtained would be exactly the same as if the mixture had been completely melted and then brought to equilibrium in a thermostat set at the eutectic temperature.

The eutectic temperature can be found by determining the freezing point of the liquid collected in G. This determination is comparatively simple, since the temperature should remain constant during freezing until the sample is practically completely solidified.

With systems showing simple compound formation there would be two eutectics, and these could be determined by using the same procedure on two samples, one rich in A and the other in B. The formation of solid solutions would cause deviations from the true diagram.

Results

Table I shows the agreement in the benzene-naphthalene system between the results obtained by the use of centrifugal filtration tubes and those determined by the more accurate freezing-point method (*1*). The benzene used was purified by repeated recrystallization and the final product had a freezing point of 5.5° C. The naphthalene was purified by sublimation and melted at 80.0° C.

Table I—Rough Construction of Benzene-Naphthalene System

C_6H_6	$C_{10}H_8$	Mol Fraction C_6H_6	Temp. before Centrifuging	Mother Liquor	Solid Phase Left	Mol Fraction C_6H_6 in Mother Liquor: Expt.	Theoret. (*1*)	Diff.
Grams	*Grams*		° *C.*	*Grams*				
5.29	21.15	0.291	12.8	7.40	$C_{10}H_8$	0.804	0.788	+0.016
7.272	7.868	0.603	−10[a]	9.155	$C_{10}H_8$	0.864	0.875	−0.011
7.272	7.868	0.603	25.5	12.285	$C_{10}H_8$	0.704	0.700	+0.004
3.985	7.885	0.453	−14[a]	4.645	$C_{10}H_8$	0.908	0.875	+0.033
3.985	7.885	0.453	50.5	10.285	$C_{10}H_8$	0.509	0.454	+0.055

[a] Determinations of eutectic composition. Eutectic temperature, −3.5° C.

Two cryohydric points were also determined and the results are shown in Table II. Merck's "Highest Purity" sodium nitrate and Mallinckrodt's C. P. potassium iodide were used to make up these solutions.

It was found in preliminary experiments that the best results are obtainable when there are approximately equal amounts of the solid phase and of the mother liquor to be separated. Thus the large deviation in the case of the last determination in Table I is probably due to the fact that the solid fraction consisted of only 1.5 grams—that is, only 10 per cent of the whole sample. In general the method is accurate to within 3 or 4 per cent. It will be shown in forthcoming papers that this compares quite favorably with the accuracy often attained by the ordinary Beckmann freezing-point method when applied to organic binary systems.

Table II—Estimation of Composition at Cryohydric Points
(Temperature before centrifuging, −70° C.)

Solute	Wt. of Solute	Wt. of H_2O	Concn. of Solute	Eutectic Temp.	Mother Liquor	Solid Phase	Solute in Mother Liquor: Expt.	Theoret.	Diff.
	Grams	*Grams*	*Wt. %*	° *C.*	*Grams*		*Wt. %*	*Wt. %*	*Wt. %*
KI	20.0	11.02	64.5	−23.2[a]	21.231	KI	48.1	51.9[a]	−3.8
$NaNO_3$	15.85	12.05	56.8	−17.5[b]	19.595	$NaNO_3$	38.5	38.4[b]	+0.1

[a] Kremann and Kershbaum, *Z. anorg. Chem.*, **56**, 218 (1907).
[b] Rodebush, *J. Am. Chem. Soc.*, **40**, 1204 (1918).

Acknowledgment

The senior author wishes to express his thanks for grants from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences and from Curtis H. Veeder, which have made this and other investigations possible.

Literature Cited

(1) International Critical Tables, Vol. IV, p. 177.
(2) Skau, *J. Phys. Chem.*, **33**, 951 (1929).

New Substrates for Use in Detecting Proteolytic Activity[1]

Robert L. Jones

Frederick Stearns and Co., Detroit, Michigan

By a modified technic, adsorption systems of egg albumin and dyes have been prepared which function as excellent qualitative reagents for determining proteolytic activity. Several albumin-dye reagents have been prepared, two of which have given good results when tested with commercial pepsin, trypsin, and artificial gastric and pancreatic juices. The method of preparation and results of the tests with egg albumin–iodoeosin and egg albumin–basic fuchsin are given. These materials are more easily prepared than carmine-fibrin or Congo red–fibrin, and being dry powders, are stable indefinitely under ordinary laboratory conditions.

COLORIMETRIC procedures for establishing the presence of proteolytic enzymes in various fluids have long been in use. The substrates used consist of some class of protein with which is incorporated a dye in such a manner that digestion of the former releases the latter and imparts a color to the system. This release of color is therefore dependent upon the presence of some enzyme which will digest the protein—i. e., the presence of free coloring matter in the system is taken as a positive test for proteolysis. Carmine-fibrin and Congo red–fibrin, which are often used in routine laboratory instruction in physiological chemistry, are familiar examples of such materials which function on the above principle.

Fibrin, a derivative of fibrinogen and possessing in general the properties of the globulins, is not water-soluble. Therefore, the preparation of carmine-fibrin and Congo red–fibrin depends simply upon soaking the fibrin in a dilute acid or alkaline solution, respectively, and gives rise to an adsorption system in which the dye is largely held upon the surface of the insoluble protein. By using a protein such as egg albumin, which can be dispersed in water, protein-dye combinations which simulate true absorption have been prepared. These substrates, which have been produced by coagulation of the protein in a colloidal system containing the dye, function as excellent preparations for demonstrating proteolytic activity. Dispersion and subsequent coagulation of the protein give more intimate contact with the dye and a firmer combination of the two. The experimental results indicate that protein-dye combinations thus prepared contain a larger proportion of dye, and that it is more uniformly released as digestion proceeds.

Preparation of Substrates

Merck egg albumin, scales, and native egg albumin have been used in the preparation of these substrates, the general method of preparation being as follows: To a 3 per cent solution (colloidal system) of dried egg albumin or a 1 to 4 aqueous dilution of fresh egg albumin, the appropriate dye was added to a concentration of 0.1 per cent. A trace of acetic acid was added and the system coagulated by heating to 80° to 90° C. The highly colored coagulum which separated was filtered off by suction and air-dried on a porous plate for 12 hours. This dried material was then reduced to a coarse powder, and washed by shaking five to six times with either 0.30 per cent hydrochloric acid or 0.25 per cent sodium carbonate. The solution used for this washing was dependent upon the type of proteolytic ferment for which the material was to be used as a test—i. e., whether active in a dilute acid or a dilute alkaline medium. The first drying was apparently necessary to set the dye and prevent the later liberation of color by either dilute acid or dilute alkali in the absence of proteolytic enzymes.

Study of Dyes

Based on the general procedure outlined above, 5 dyes were studied. These were chosen with respect to depth of color, relative acid or alkali fastness, and minimum degree of re-adsorption by the peptized albumin. All tests were run in a water bath at a temperature of 52° C., using approximately 1 gram of substrate. The amounts of digestive ferments used were considerably in excess of the minimum requirements. The object in this series of tests was to determine the utility of such egg albumin–dye substrates as qualitative tests for proteolytic enzymes, with no attempt at ascertaining the sensitivity of the method. This phase of the subject will be touched upon later, in connection with comparative results obtained with egg albumin–dye and fibrin-dye substrates. Control tests, tubes with no digestive ferment added, were run simultaneously. The following results were obtained.

(1) Egg Albumin–Gentian Violet—This combination, tried with one part of 1:3000 commercial pepsin to approximately 100 parts of substrate, showed pronounced release of color within 30 minutes. The depth of color produced was not suitable for a colorimetric procedure and there was considerable re-adsorption of the liberated dye by the peptized albumin. The control tubes also showed a considerable release of color.

(2) Egg Albumin–Malachite Green—This absorption system under conditions identical with those in (1) gave very similar results. Although the amount of re-adsorption was not as pronounced as with gentian violet, the degree of color produced was not sufficient. There was an appreciable release of color in the control tubes.

(3) Egg Albumin–Iodoeosin—This dye was the most satisfactory of any tried in acid systems. When the ratio of 1:3000 commercial pepsin to substrate was 1 to 100, a deep pink color was apparent in 30 minutes in 0.30 per cent hydrochloric acid solution. This color was permanent for 8 hours and there was no liberation of dye in the control tubes over this interval. Excellent results were obtained with this material in artificial gastric juice (*1*).

(4) Egg Albumin–Basic Fuchsin—This substrate gave very satisfactory results in a 0.25 per cent sodium carbonate solution, using one part of 1:25 trypsin to five parts of substrate. A deep color was imparted to the solution in 35 minutes and no color was released in the control tubes. The permanence of the color indicated that re-adsorption was very slight. In 20 cc. of 0.25 per cent sodium carbonate containing 3 cc. of artificial pancreatic juice (*2*), egg albumin–basic fuchsin gave more positive results in a shorter

[1] Received November 13, 1930. Presented before the Division of Biological Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Table I—Comparison of Color Liberation from and Digestion of Protein-Dye Substrates by Proteolytic Enzymes

No.	Substrate[a]	Enzyme	Color			Nitrogen in Substrate-Free Filtrate		
			Start	30 minutes	60 minutes	Start	30 minutes	60 minutes
						Mg./cc.	*Mg./cc.*	*Mg./cc.*
1	Egg albumin-iodoeosin	1 part per 1000 of 1:3000 commercial pepsin	Colorless	Reddish pink	Deep pink	0.02	0.19	0.27
2	Egg albumin-iodoeosin	None	Colorless	Colorless	Colorless	0.04	0.04	0.05
3	Carmine-fibrin	1 part per 1000 of 1:3000 commercial pepsin	Colorless	Deep pink, opalescent	Deep pink, very opalescent	0.03	0.61	0.70
4	Carmine-fibrin	None	Colorless	Faint pink	Pronounced pink	0.04	0.09	0.13
5	Egg albumin-basic fuchsin	1 part in 8 of 1:25 trypsin	Colorless	Deep orchid	Intense purple	0.06	0.10	0.16
6	Egg albumin-basic fuchsin	None	Colorless	Colorless	Colorless	0.03	0.03	0.05
7	Congo red-fibrin	1 part in 8 of 1:25 trypsin	Colorless	Deep pink, very opalescent	Light red, very opalescent	0.07	0.59	0.96
8	Congo red-fibrin	None	Colorless	Slight opalescence	Opalescent, faint pink	0.03	0.06	0.07

[a] One-gram portions.

interval of time than in 1 per cent commercial trypsin solutions.

(5) Egg Albumin–Gentian Violet—Results with this material in dilute alkaline solutions containing commercial trypsin were unsatisfactory. A pronounced opacity developed in the tubes containing the proteolytic enzyme, but there was little depth of color, indicating a rapid re-adsorption of the dye by the peptized albumin.

(6) Egg Albumin–Methylene Blue—This substrate, under conditions identical with (5), behaved very similarly, and the results secured were unsatisfactory for the same reasons.

Of the 5 egg albumin–dye substrates investigated, two, egg albumin–iodoeosin and egg albumin–basic fuchsin, were found to give very pronounced colorimetric tests for enzymes of the peptic and tryptic type, respectively. Accordingly, these two reagents were compared with carmine-fibrin and Congo red–fibrin as qualitative tests for pepsin and trypsin. Comparisons were made of the degree of color release from these protein-dye substrates and the degree of digestion as indicated by the amount of nitrogen in the substrate-free filtrate from each test. All tests, together with controls, were run simultaneously in test tubes immersed in a water bath at 52° C. The results are given in Table I. Tubes number 2, 4, 6, and 8 were the controls, containing no digestive enzyme.

Experimental Procedure

Egg albumin–iodoeosin and egg albumin–basic fuchsin were prepared according to the method previously given. The fibrin-dye substrates were prepared according to the usual method (*3*), using Difco purified, desiccated blood fibrin. Since fibrin preparations are kept under glycerol, whereas the albumin substrates were prepared dry, it was necessary, in order to obtain comparable amounts of each, to soak them for $^1/_2$ hour previous to use in either 0.30 per cent hydrochloric acid or 0.25 per cent sodium carbonate. The substrates were then filtered on a Büchner funnel and 1-gram portions weighed out for each test. Since the protein-dye materials were weighed moist, the proportion of enzyme to substrate, as stated in Table I, is not accurate. All figures are on the same relative basis, however, and are none the less comparable. To these portions of substrate, 20 cc. of 0.30 per cent hydrochloric acid or 0.25 per cent sodium carbonate containing the correct amount of pepsin or trypsin, respectively, was added.

In the determination of nitrogen 2-cc. portions of the liquid above the substrate were withdrawn, filtered immediately, and nitrogen determined therein by a modification of the Koch-McMeekin (*4*) method for nitrogen in blood.

These nitrogen determinations are given for substrate-free filtrate. With both fibrin preparations a pronounced opacity, due to finely divided protein particles, developed within 30 minutes. At least a portion of this colloidal material passed through the filter paper. Therefore the determinations were not made on protein-free filtrate. The peptized fibrin in the 2 cc. of filtrate, though still possessing protein characteristics, is in a sense an index of degree of digestion of the substrate. The nitrogen figures throughout may not be comparable, since a certain portion of undigested protein nitrogen is represented in the filtrates from the fibrin substrates, whereas the increase in nitrogen in the filtrates from the albumin substrates is probably due to actual digestion.

It appears that liberation of color from fibrin-dye combinations is due to peptizing of the fibrin, the finely divided particles carrying the color and imparting a decided opacity to the system. With egg albumin–dye combinations, no opacity develops and the liquid above the substrate takes on a considerable depth of color. This release of color in the latter case appears to be dependent upon proteolysis, since in the controls (numbers 2 and 6 of Table I) there was no release of color and no increase in nitrogen content of the substrate-free filtrate over a period of 1 hour.

With respect to the sensitivity of these modified substrates no definite conclusions can be drawn, since only two amounts of pepsin and trypsin were used. In the first attempted comparative test of egg albumin–iodoeosin with carmine-fibrin and egg albumin–basic fuchsin with Congo red–fibrin, one part of 1:3000 pepsin to 3000 parts of substrate, and one part of 1:25 trypsin to 25 parts of substrate were used. The color developed in 60 minutes with any substrate was barely perceptible, certainly not sufficient for a qualitative test. When three times these amounts of ferments were used, the results given in Table I were secured. It appears probable, therefore, that under the conditions of these experiments sensitivity of the fibrin-dye and albumin-dye substrates is not materially different and lies somewhere between the two levels run—i. e., well under the maximum range of peptic and tryptic activity.

Conclusions

Although re-adsorption of the dye by the peptized protein is a factor of considerable magnitude in some protein-dye adsorption systems, the results herein presented show that it is possible to select dyes in which this factor operates at a minimum. These results also demonstrate the possibility of preparing protein-dye combinations which are fast to acid or alkali under the conditions required for the optimum activity of peptic and tryptic enzymes, and in which the release of color is dependent solely upon proteolysis.

In the air-dried condition in which these materials are prepared, it has not been found necessary to use special care or methods in their preservation. Samples which have

been kept in stoppered reagent bottles under ordinary laboratory conditions have shown no evidence of decomposition or loss of reactivity over a period of several months.

In addition to their keeping qualities under ordinary laboratory conditions, egg albumin–iodoeosin and egg albumin–basic fuchsin fulfill the necessary conditions with respect to minimum degree of re-adsorption and acid or alkali fastness. These advantages, together with their relative ease of preparation, demonstrate their possibilities in qualitative tests for proteolytic activity and lead to the belief that such substrates will be found more satisfactory than carmine-fibrin and Congo red–fibrin.

Literature Cited

(1) Hawk, P. B., and Bergeim, Olaf, "Practical Physiological Chemistry," p. 210, Blakiston, 1926.
(2) Hawk, P. B., and Bergeim, Olaf, *Ibid.*, p. 259.
(3) Hawk, P. B., and Bergeim, Olaf, *Ibid.*, p. 56.
(4) Koch, F. C., and McMeekin, T. L., *J. Am. Chem. Soc.*, **46**, 2066 (1924).

Absolute Determination of Nitrogen in Organic Compounds[1]

Pregl's Micro-Method

Otto R. Trautz and Joseph B. Niederl

Department of Chemistry, New York University, New York, N. Y.

The accuracy of Pregl's micro-Dumas method may be increased by using measured amounts of carbon dioxide and copper oxide, and applying empirical corrections for air and absorption errors. Wall adhesion (0.5 per cent of the nitrogen volume collected) and vapor pressure of the potassium hydroxide solution are considered.

OF ALL the methods in organic microanalysis the absolute nitrogen determination enjoys perhaps the greatest use and the field of its application in organic and biological as well as in industrial research is steadily increasing. Quite a number of investigations have been dealing with the various phases of the method in order to explain and eliminate sources of error. The following comprehensive description of the analytical apparatus and procedure may be of assistance, therefore, to those availing themselves of this reliable and quick method for the determination of nitrogen.

Apparatus

The analysis train, as shown in Figure 1, consists of a Kipp carbon dioxide generator, gasometer, combustion tube, *CT*, two-way stopcock, *E*, and precision azotometer. The acid of the Kipp must be guarded from contact with air in order to keep the degree of purity of the carbon dioxide constant. The Kipp of Figure 1 can be evacuated and can then deliver carbon dioxide containing only 0.001 cc. impurity in 100 cc. carbon dioxide. Other satisfactory arrangements are described by Niederl, Trautz, and Saschek (*4*), and by Lindner (*3*), Diepolder (*1*), and Hein (*2*). The combustion tube and the azotometer are filled according to directions given by Pregl (*5*).

[1] Received November 20, 1930. Presented under the title "Improvements in the Micro-Dumas Method" before the Division of Physical and Inorganic Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 8 to 12, 1930.

Method

A sample of 3 to 5 mg. is weighed on a standard microchemical balance (sensitivity 0.001 mg.), or on an ordinary analytical balance (sensitivity 0.1 mg.) making use of the dilution method (*4*). For the introduction of the sample into the combustion tube Pregl's (*5*) instructions are followed, care being taken that for each analysis the same amounts of the coarse and especially of the fine copper oxide are used.

Then the air in the combustion tube must be eliminated by passing one gasometer charge of carbon dioxide through the system while cold (stopcock *E* open to the atmosphere). If near the end of this operation, which should require about 5 minutes, stopcock *E* is opened to the azotometer, small micro-bubbles (not larger than 0.2 of one division) should appear in the azotometer.

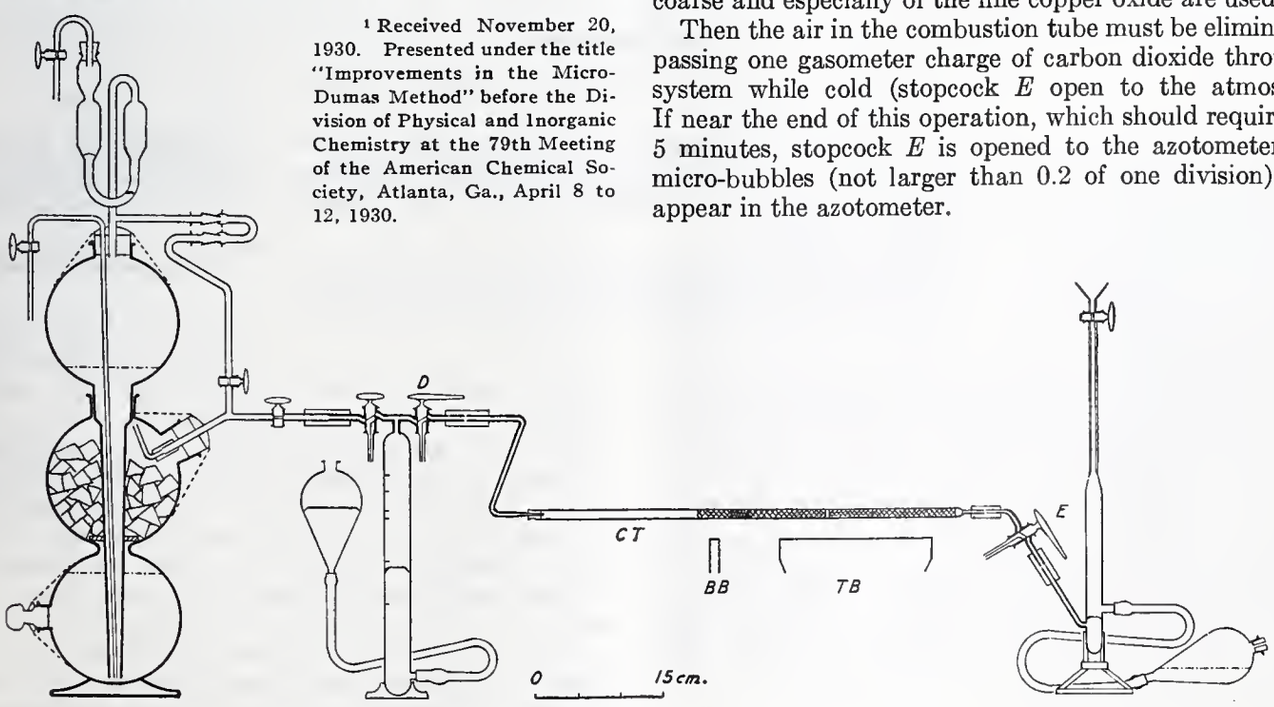


Figure 1—Diagram of Apparatus

In the next operation, the actual combustion, stopcock *D* of the gasometer is closed, stopcock *E* opened to the azotometer, the long burner *TB* is lighted, and the combustion tube heated to red heat. Then the Bunsen burner, *BB*, is lighted, the heating of the temporary charge is started at the empty portion of the tube, and the flame gradually moved nearer and nearer to the long burner. The rate at which the bubbles enter the azotometer must not exceed 2 bubbles in 3 seconds, and this rate is carefully regulated by the proper movement of the burner.

During the combustion the gasometer is refilled with carbon dioxide to a mark between 50 and 100 cc. (50 cc. have been found to be sufficient).

When no more bubbles rise in the azotometer, the combustion is at an end and the gaseous combustion products must be conveyed into the azotometer by a current of carbon dioxide; stopcock *D* is carefully opened and adjusted to give a rate of one bubble per second for the 10 minutes. During this the temporary charge is again heated throughout with the Bunsen burner to insure complete combustion. The burner is moved in the same direction as before and then extinguished. The remainder of the gasometer charge can be passed through the system at a higher rate, about 3 bubbles per second, and as soon as the current of gas has ceased, because of the absence of pressure in the system, stopcock *E* is closed and the long burner extinguished.

After 15 minutes, the readings are taken of the nitrogen volume in the azotometer, to within 0.001 cc., with the potassium hydroxide leveling bulb at the height of the meniscus, and of its temperature to within 0.5° C., with the bulb of the thermometer touching the wall of the measuring capillary, and of the barometric pressure to within 1 mm.

In order to determine the air and absorption errors—i. e., that volume of gas collecting in the azotometer during an analysis, which originates from the air content of the carbon dioxide used and from air absorbed to the temporary charge—a blank analysis is carried out combusting a nitrogen-free substance (a few milligrams of pure cane sugar) in exactly the same way as in the actual analysis. The sum of the air and absorption errors is deducted from the azotometer readings obtained in the actual analyses and should be determined as often as any changes in the Kipp apparatus or in the procedure of the analysis are made.

Calculation

To the volume reading, the calibration correction of the azotometer (from the apparatus certificate) is first applied. From the resulting volume deduct: (*a*) the correction for air and absorption errors (from the blank analysis); (*b*) 1.1 per cent—i. e., 0.5 per cent for adhesion of the potassium hydroxide to the wall, thus reducing the volume of the gas in the capillary of the azotometer (*6*); 0.3 per cent for the vapor pressure of the potassium hydroxide solution (50 per cent); 0.3 per cent (approx.) for the temperature reduction of the barometer reading (from 18° to 0° C.).

The resulting nitrogen volume is reduced to normal conditions (760 mm. and 0° C.) and the percentage of nitrogen calculated.

o-Toluamide sample, mg.		3.475
Collected nitrogen, cc., (at 24.5° C. and 767 mm.)		0.321
Calibration correction, cc.	0.001	
Air and absorption correction, cc.	0.008	
1.1 per cent correction, cc.	0.003	
Total corrections		0.012
Net volume nitrogen to be reduced to normal conditions, cc.		0.309
Nitrogen found, %		10.33
Nitrogen calcd., %		10.37

Literature Cited

(1) Diepolder, *Chem.-Ztg.*, **43**, 353 (1919).
(2) Hein, *Z. angew. Chem.*, **40**, 864 (1927).
(3) Lindner, *Ber.*, **59**, 2806 (1926).
(4) Niederl, Trautz, and Saschek, *Mikrochemie*, Emich Festschrift, 227 (1930).
(5) Pregl, "Quantitative Organic Microanalysis," Blakiston, 1924; Springer, 1930.
(6) Trautz, *Mikrochemie* (1931).

Measurement of Consistency of Starch Solutions[1]

J. C. Ripperton

Hawaii Agricultural Experiment Station, Honolulu, Hawaii

A study of the swelling of starches and its relation to viscosity has been made and a method of evaluating starches by the swell method using a very simple apparatus devised.

This method is applicable chiefly to the tuber starches with a large swell, such as those of potato, sago, arrowroot, and to a lesser extent to cassava starch.

The consistency of starch solutions is quite generally determined by some type of viscometer or plastometer. These vary in principle and design, but they have as their purpose the measurement of the internal resistance to flow of the viscous or plastic solution. Emulsoid colloids, such as starch, owe a large part of their viscous properties to swelling on imbibition of water. Determination of this ability to swell was used by Harrison (*1*) as a measure of the consistency of the starch solution. Measurement of the swelling of starch as an index of its strength has been used occasionally but has never received general recognition. In the course of an investigation to determine the relative properties of edible canna and potato starches, a study was made of the swelling method and its relation to viscosity. The method described, which has certain advantages over the viscosity methods ordinarily used, was developed for factory control purposes.

[1] Received November 7, 1930.

Preparation of Solution

It is well known that starch exists as granules, rather than as a homogeneous powder. When heated with water these granules imbibe water and swell greatly. In the natural starches, each granule exists as an inflated balloon consisting of a skin, called amylopectin, and a milky colloidal liquid within, called amylose. If the solution is sufficiently dilute, the swollen starch grains will settle on standing, leaving a clear supernatant liquid. With increasing concentration, the granules fill more and more of the space until no settling can occur. The starch solution begins to take on noticeable viscosity when the swollen granules fill all the liquid space. It is common knowledge that when a starch solution is stirred or agitated vigorously it becomes less viscous and can

finally be reduced to a watery consistency. This has been shown to be owing to the bursting of the granules.

Herein lies one of the chief difficulties in the development of methods for determining the consistency of starch solutions, especially with respect to the large-granuled tuber starches. The cereal starches have a smaller swell and a larger proportion of amylopectin and are not so subject to change. The greatly inflated granules of such starches as potato are very tender and easily broken by agitation and stirring. They will burst of their own accord if heated at boiling temperatures for any length of time. Any method

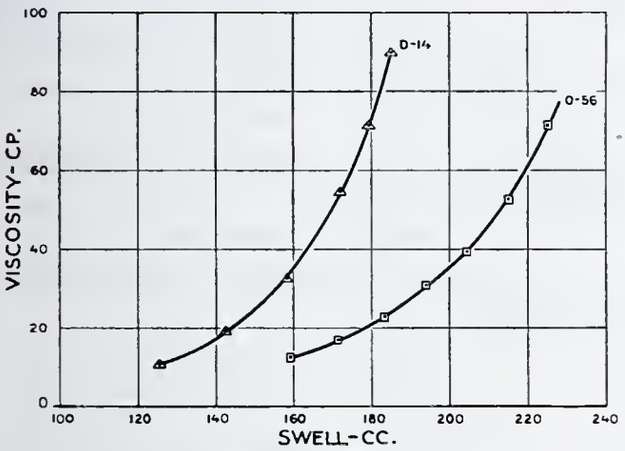


Figure 1—Relation of Viscosity to Swell

for the determination of the strength of a starch must take into account this breaking of the starch grains in order to duplicate results. Nivling (*2*) contends that the only viscosity measurement that has any significance in practical work is that reached after prolonged cooking has reduced it to a constant value. Most investigators seek to obtain the initial viscosity of the starch by adopting an arbitrary procedure whereby the amount of granules broken during the preparation of the solution is always the same. For example, Wolff (*3*) brings the starch into solution by heating over a steam bath and then boils the solution over a naked flame for exactly $2^1/_2$ minutes.

The following method was developed to bring the starch into solution with the least probability of breaking the granules: A series of 125-cc. Erlenmeyer flasks, varying no more than 6 or 8 grams in weight are selected. The sample of air-dry starch is weighed into the Erlenmeyer and 10 cc. of distilled water added. Distilled water at exactly 97° C. is rapidly drawn up into a 100-cc. pipet whose tip has been filed off to about a 3-mm. opening. The starch is then brought into solution by allowing the hot water from the pipet to run rapidly into the starch suspension. The tip of the pipet is kept in the center of the flask and just below the rising level of the liquid. This produces a rolling motion of the liquid, down in the center, out at the bottom, up on the outside, and in at the top. The entire 100 cc. of hot water are delivered into the flask in about 10 seconds. The final temperature of the solution is 80° ± 0.5° C. The starch granules are thus kept perfectly dispersed during the time they are swollen. The granules do not reach their maximum swell for several minutes, so that during the addition of the hot water they are quite mobile, and perfect solution is produced without any stirring.

It is obvious that radiation takes place rapidly during the filling of the pipet and delivery of the hot water into the solution. However, by following a uniform and rapid procedure, the final temperature of the starch solution in the flask will not vary more than 0.5° from 80° C. The distilled water is kept at 97° C. in a liter Florence flask over a small flame. A thermometer inserted through a rubber stopper is kept in the water, the tip being near the center. To make the final adjustment of exactly 97° C., the flask is either heated for a few moments over a naked flame if too low, or removed from heat entirely until by constant swirling of the contents the exact temperature is reached. The stopper and thermometer are then quickly removed, the tip of the pipet inserted to near the center of the liquid, and the pipet quickly filled. After each removal more water is added so that the flask is kept nearly full at all times.

Cooking

As soon as the starch has been brought into solution, a loose cotton plug is placed in the mouth of the Erlenmeyer, and the flask placed in a water bath for 15 minutes at 80° C. A longer time causes a gradual increase in the swell, but the relative difference between starches remains about the same. The water in the bath is kept nearly to the top of the flasks which are held down with lead collars. The solutions are not stirred or shaken during any part of the process.

With starches such as potato and edible canna, cooking may be dispensed with. Instead, the starch solution is simply allowed to stand at room temperature for at least 15 minutes. Longer time of standing has no effect on the results.

Measurement of Swell

The swell of the starch is measured in lipless cylinders of about 400 cc. capacity with a rim around the top.[2] About 200 cc. of distilled water are measured into each cylinder. After cooking or standing for 15 minutes, the starch solution is poured into the cylinder. The flask is rinsed with a few cubic centimeters of water which is also poured into the cylinder. The exact volume of water used is of no consequence. A rubber stopper is then placed tightly in the top and the cylinder is carefully inverted twice, but not shaken. It is then allowed to stand undisturbed overnight. The next

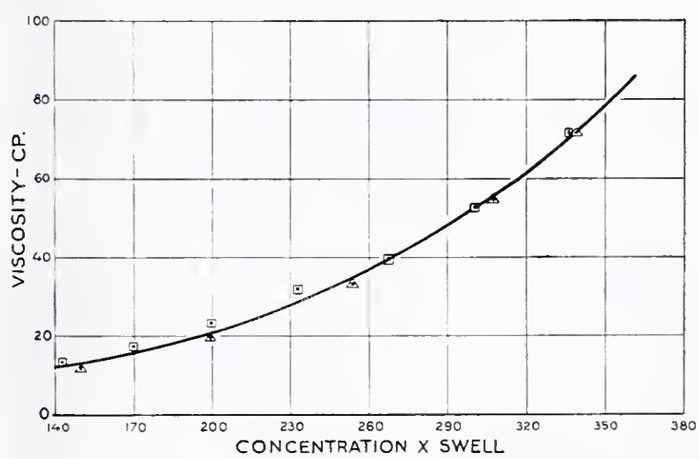


Figure 2—Relation of Viscosity to Concentration × Swell

morning the volume or swell of the starch granules is measured. This can be read off from graduations on the side of the cylinder or by bringing the edge of a strip of paper, held by a rubber band, to the exact level of the settled starch grains. The contents of the cylinder are poured out, water added to the exact level of the strip of paper, and the volume of the water thus used measured in a graduate.

Relation of Swell to Viscosity

To determine the relation of the swell of a starch to its viscosity, determinations were made on different concentrations of the cooked samples in a Stromer viscometer at 80° C. The instrument was standardized with sucrose so that time seconds could be expressed as centipoises. The relation of

[2] Similar to Catalog No. 4392, A. H. Thomas Company, 1921 edition.

viscosity, expressed in centipoises, to swell is shown in Figure 1 for two commercial samples[3] of potato starch. D-56 represents a starch of unusually high viscosity, and D-14 one of medium viscosity. It will be noted that a much greater swell of D-56 is required to produce a given viscosity than of D-14. This means that starches differ in the relation of swell to viscosity, hence the swell cannot be taken as a direct measure of the viscosity. If, however, the viscosity is plotted against the product of the concentration times the swell (Figure 2), the curves of D-14 and D-56 practically coincide. By this means a direct relationship between swell and viscosity is obtained. For example, if a 1.5-gram sample gave a swell of 150 cc.,

$$1.5 \times 150 = 225 \text{ (concentration} \times \text{swell)}$$

This, referred to Figure 2, gives a viscosity of 26 centipoises.

It has been suggested by Wolff (*3*) that for practical work the viscosity values of different starches should be expressed in terms of a standard starch rather than in absolute viscosity units. This method seems decidedly advantageous for the reason that the viscosity value obtained for a given starch is relative. A slight difference of procedure in preparing the solution will give a different viscosity. Air-dry starch is very stable in its properties and makes a dependable standard over a period of years.

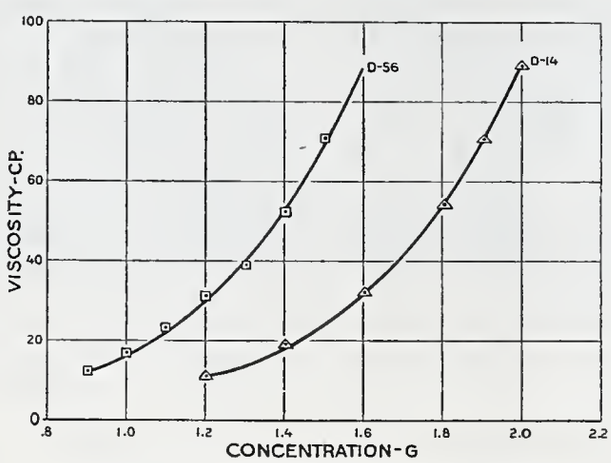


Figure 3—Relation of Viscosity to Concentration

Viscosities of the standard starch are determined for a series of different concentrations. Plotting these values gives a curve similar to those in Figure 3. To evaluate an unknown starch, the viscosity of any concentration is determined. The ratio of this concentration to that of the standard required to give the same viscosity is the value of the unknown with respect to the standard. For example, taking D-14 as the standard starch, 1.6 grams of the unknown starch gave a viscosity of 24 centipoises. Twenty-four centipoises on the standard curve are equivalent to

$$1.5 \text{ grams. } 1.5 \div 1.6 = 94 \text{ per cent}$$

the value of the unknown starch (standard starch = 100). Determinations of the viscosity of the standard starch will often vary somewhat above or below that of the standard curve owing to small differences in procedure, impurities in the distilled water, etc. To correct for this, viscosity is determined in samples of the standard starch and the unknown starch at the same time, and the correction applied as follows: 1.6 grams of the standard starch gave a viscosity of 36 centipoises. This is equivalent to 1.64 grams on the standard curve. The corrected value of the unknown starch in the previous example would then be as follows:

$$1.5 \div 1.64 = 91 \text{ per cent}$$

By using the same method it is possible to evaluate the unknown in terms of the standard from the values of the swell by referring the viscosity in centipoises obtained from Figure 2 to the standard curve in Figure 3.

Evaluating a Starch without Use of Viscometer

Where a viscometer is not available, for practical work the swell may be used to determine the value of a starch in terms of the standard by the use of the curve in Figure 2 and the D-14 curve in Figure 3 without establishing the viscosity values for the particular starch which is to be used as a standard. For example, suppose 1.6 grams of the starch selected to be the standard (S) has a swell of

$$170 \text{ cc. } 1.6 \times 170 = 272$$

which is equivalent to 41 centipoises. 1.6 grams of the unknown starch (X) has a swell of

$$135 \text{ cc. } 1.6 \times 135 = 216$$

which is equivalent to 24 centipoises. Referred to the D-14 curve (Figure 3),

$$41 \text{ cp.} = 1.69 \text{ grams}$$

and

$$24 \text{ cp.} = 1.5 \text{ grams}$$
$$1.5 \div 1.69 = 88 \text{ per cent}$$

the value of X in terms of S. This method may also be used when the swell is determined without cooking, since the effect would be relatively the same for the standard as for the unknown.

It is thus possible, in a practical way, to evaluate starches by the swell method with very simple apparatus—namely, flasks, pipets, and cylinders.

Importance of Cleanliness

In any determinations of the consistency of starch solutions, special attention must be given to cleanliness of the apparatus. The minutest trace of salts getting into the solution from the glassware, or differences in the purity of the distilled water, affect the results. Although these effects are partially compensated by testing the standard starch along with the unknown, special care should also be used. For example, the distilled water left in the hot-water flask from one day should be discarded and the flask filled with fresh distilled water. The Erlenmeyer flasks and cylinders should be carefully brushed clean, then rinsed repeatedly with distilled water, and stood upside down on pegs to drain. At least three determinations should be made and the average value taken.

Literature Cited

(1) Harrison, W., *J. Soc. Dyers Colourists*, **27**, No. 4, 84–8 (1911).
(2) Nivling, W. A., "Significance of Starch Viscosity in the Manufacture of Paper and Textiles. A Comprehensive Survey of Starch Chemistry," Vol. I, edited by R. P. Walton, 1928.
(3) Wolff, O., *Chem.-Ztg.*, **103**, 1001, 1012 (1927).

[3] These were selected from a series of commercial starches obtained through courtesy of Joseph Morningstar & Co., New York.

Timber and Wood Pulp Combine in Sweden

Ten independent Swedish timber and chemical wood pulp companies, representing a share capital of nearly $20,000,000 with a total annual output of 316,000 tons of wood pulp and about 135,000 standards of timber, have formed a joint sales and purchasing organization. The mills retain complete independence and the understanding does not affect the management in any way.

Unit Coal Studies on Some Virginia Coals[1,2]

F. H. Fish and J. A. Addlestone

Department of Chemistry and Chemical Engineering, and the Engineering Experiment Station, Virginia Polytechnic Institute, Blacksburg, Va.

Parr's formula for unit coal B. t. u. and Fieldner's modification of this formula have been applied to analytical data on coal from ten Virginia seams, including float and sink portions of these coals. Twenty-eight samples from different parts of the Merrimac seam were also calculated to unit coal B. t. u. by these formulas.

The calculated values were not in so good agreement as could be expected until correction was made for the carbon dioxide content of these coals. When the Parr and Fieldner formulas are modified to take this factor into account, the unit coal B. t. u.'s are in closer agreement. For the twenty-eight samples from the same seam, the average deviation from the mean is ±75 B. t. u. by the Parr formula and ±86 B. t. u. by the Fieldner modification of this formula. For the other coals studied, the average of differences in unit B. t. u. between the untreated, float, and sink portions of each coal is 82 B. t. u. by the Parr formula and 96 B. t. u. by the Fieldner formula.

Parr's classification of coal (*6*) is based on the calorific values of his unit coal or pure coal in which the mineral matter has been eliminated. Since the elementary composition of coals of the same kind varies between narrow limits, it appears that the elementary composition of pure coal is the best basis for classification of coals from the standpoint of chemical composition.

Unit coal is defined by Parr (*5*) as the "organic material which is involved in combustion as apart from the mineral constituents which are the extraneous and variable accompaniments of the actual or unit coal." The types of mineral constituents associated with the coal are in the form of ash, shale and clay residues, pyrites, and carbonates. By eliminating these various non-coal constituents, we arrive at the actual coal substance.

Of the various formulas in use for correcting the calorific value of coal to an ash-free basis the most commonly used is:

$$\text{B. t. u. (corrected)} = \frac{\text{Indicated B. t. u.}}{1.00 - \text{ash}} \qquad (1)$$

This formula assumes that the ash as determined by ordinary analysis is identical in amount with the original mineral matter in the coal. However, the ash as determined is always less in amount than the original mineral matter in the coal. This causes the correction to be too small.

Parr has derived a formula for correcting analyses to the basis of pure coal which takes into consideration this fact. The formula suggested is

$$\text{Unit B. t. u.} = \frac{\text{Indicated B. t. u.} - 5000\,S}{1.00 - (1.08\,\text{ash} + 22/40\,S)} \qquad (2)$$

The value 5000 S indicates the heat due to the combustion of the sulfur in the form of pyrites to ferric oxide. The value 22/40 S in the denominator is obtained from consideration of the atomic ratio of the oxygen of the ash combined as ferric oxide to the total sulfur which it replaces. The factor 1.08 is a correction for the water of hydration of the clay and shaly constituents of the ash, which is lost during the ash determination.

This formula assumes all of the sulfur to be in the form of pyrites which is not exactly true. The factor 1.08 was derived from a study of shales associated with some Illinois coals and probably varies in amount with different coals.

Fieldner and Selvig (*3*) suggest a modification of Parr's formula in which one-half the sulfur is assumed to be present as pyrite and one-half as organic. This formula is as follows:

$$\text{Unit B. t. u.} = \frac{\text{Indicated B. t. u.} - 4650\,S}{1.00 - (1.08\,\text{ash} + 3/4\,S)} \qquad (3)$$

It is the purpose of the present investigation to determine which formula may be best used in correcting ash to obtain unit B. t. u. for some Virginia coals. The formulas as stated above are to be applied to analytical data of the various coals on the moisture-free basis.

Experimental Procedure

To test the correctness of the various formulas as applied to the coals under investigation, the coals were subjected to a float-and-sink separation. In this way a float coal with a low ash content and a sink coal with a high ash content were obtained. If the correction factors in the unit coal formulas are adequate, the calculated unit B. t. u. for the untreated, float, and sink portions should check and be practically identical, if it is assumed that the actual coal substance is the same in the untreated, float, and sink portions.

A sample of the coal ground to 20 mesh was placed in a 2 ½-liter acid bottle and a mixture of carbon tetrachloride and benzene of specific gravity 1.35 was added. The coal was thoroughly stirred in the solution and allowed to stand 24 hours or more until a good separation was obtained. The float coal was drawn off by means of suction into another bottle, leaving the sink portion in the main part of the solution. Both samples were then filtered and allowed to dry on the filter paper in order to remove by evaporation the carbon tetrachloride and benzene.

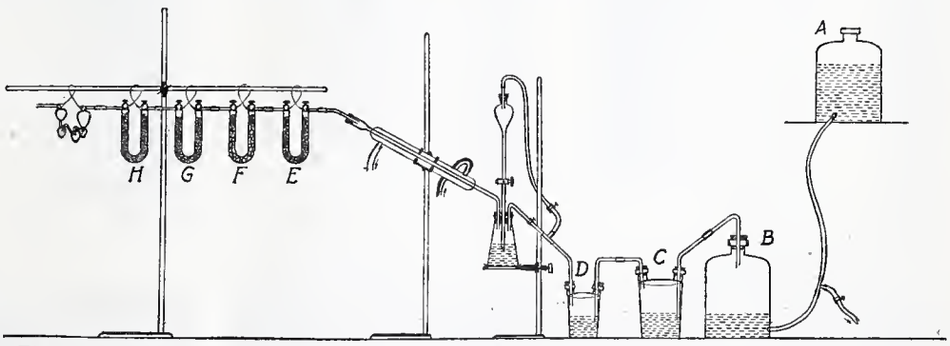


Figure 1—Diagram of Apparatus Used for the Determination of Carbon Dioxide in Coal

This method of float-and-sink separation is substantially the same as described by Bird and Messmore (*1*). The untreated, float, and sink portions of each coal were then analyzed by the standard methods.

The determination of carbon dioxide was made in a modification of the type of apparatus diagramed in Figure 1 and described by Hillebrand (*4*).

[1] Received December 8, 1930.

[2] This work is recorded in the Engineering Experiment Station of the Virginia Polytechnic Institute as a portion of Project 22.

Table I—Analyses of Some Virginia Coals with Calculated Unit B. t. u.

Seam	Condition of Sample	Ash	S	Observed B. t. u.	B. t. u. / (1.00 − Ash)	Diff.	B. t. u. − 5000 S / (1.00 − (1.08 Ash + 22/40 S))	Diff.	B. t. u. − 4650 S / (1.00 − (1.08 Ash + 3/4 S))	Diff.
		%	%							
Dorchester	Untreated	3.9	1.17	14669	15263		15356		15504	
	Float	2.9	0.98	14830	15276		15345		15383	
	Sink	15.9	4.61	12412	14760	516	15171	185	15368	136
Blair	Untreated	3.5	0.72	14670	15202		15274		15292	
	Float	2.1	0.59	14913	15233		15279		15310	
	Sink	16.2	1.04	12560	14952	281	15303	29	15309	18
Parsons	Untreated	7.2	1.12	13964	14887		15171		15223	
	Float	3.6	0.82	14479	15019		15093		15129	
	Sink	18.3	1.97	12050	14750	269	15100	78	15184	94
Low Splint	Untreated	5.9	0.79	13981	14857		14959		14988	
	Float	3.1	0.65	14339	14789		14856		14880	
	Sink	25.4	1.33	10745	14404	453	14864	103	14927	108
Taggart	Untreated	2.2	0.46	14800	15133		15176		15193	
	Float	1.0	0.46	15037	15190		15069		15233	
	Sink	13.2	0.41	12600	14517	673	14713	463	14736	497
Lower Banner	Untreated	5.7	0.65	14589	15471		15578		15595	
	Float	4.1	0.62	14800	15432		15510		15532	
	Sink	15.2	1.22	12921	15355	116	15509	69	15605	73
Upper Banner	Untreated	4.7	0.50	14488	15202		15281		15310	
	Float	2.6	0.62	14882	15295		15334		15271	
	Sink	18.8	0.78	11923	14680	615	14992	342	15026	284
Jawbone	Untreated	14.7	0.65	12599	14770		15002		15029	
	Float	4.4	0.67	14261	14919		14995		15018	
	Sink	18.5	0.68	11911	14615	304	14912	90	14940	89
Imboden	Untreated	4.1	0.92	14285	14896		14976		15001	
	Float	2.1	0.78	14655	14969		15021		15035	
	Sink	19.2	1.92	11702	14305	664	14853	158	14932	103
Merrimac	Untreated	19.1	0.60	12087	14940		15284		15280	
	Float	4.5	0.44	14674	15365		15440		15386	
	Sink	22.0	0.66	11569	14832	533	15204	236	15233	153
Av. of differences between lowest and highest B. t. u.						442		175		156

Table II—Analyses of Coals from Merrimac Seam with Calculated Unit B. t. u.

Sample	Ash	S	Observed B. t. u.	B. t. u. / (1.00 − Ash)	Devn. from Av.	B. t. u. − 5000 S / (1.00 − (1.08 Ash + 22/40 S))	Devn. from Av.	B. t. u. − 4650 S / (1.00 − (1.08 Ash + 3/4 S))	Devn. from Av.
	%	%							
1	44.2	0.37	8070	14406	−590	15466	+183	15488	+175
2	14.1	0.37	13155	15314	+318	15534	+251	15529	+216
3	15.8	0.40	12735	15124	+128	15360	+ 77	15373	+ 60
4	26.6	3.17	10620	14470	−526	15041	−242	15190	−123
5	16.1	0.44	12674	15106	+110	15360	+ 77	15379	+ 66
6	29.2	2.43	10439	14744	−252	15370	+ 87	15495	+182
7	31.5	3.71	9681	14133	−863	14851	−432	15046	−267
8	12.1	0.45	13116	14921	− 75	15104	−179	15122	−191
9	10.7	0.83	13414	15021	+ 25	15200	− 83	15320	+ 7
10	12.0	0.36	13398	15225	+229	15408	+125	15422	+109
11	12.9	0.34	13297	15266	+270	15463	+180	15480	+167
12	20.0	0.32	11486	14333	−663	14663	−620	14676	−637
13	28.9	0.32	10661	15000	+ 4	15515	+232	15530	+217
14	9.6	0.49	13827	15295	+299	15445	+162	15465	+152
15	14.8	0.44	12582	14768	−228	14991	−292	15011	−302
16	9.5	0.44	13713	15152	+156	15298	+ 15	15314	+ 1
17	13.9	0.34	12643	14684	−312	14890	−393	14898	−415
18	7.4	0.39	14179	15312	+316	15425	+142	15439	+126
19	12.2	0.32	13439	15300	+304	15491	+208	15505	+192
20	13.5	0.37	13207	15269	+273	15476	+193	15492	+179
21	14.2	0.45	12803	14922	− 74	15140	−143	15170	−143
22	14.2	0.34	13088	15254	+258	15473	+190	15482	+169
23	16.3	0.60	12423	14842	−154	15101	−182	15125	−188
24	10.9	0.35	13390	15029	+ 33	15190	− 93	15202	−111
25	9.0	0.42	13797	15162	+166	15297	+ 14	15315	+ 2
26	16.9	0.58	12743	15334	+338	15613	+330	15639	+326
27	11.0	0.39	13416	15074	+ 78	15240	− 43	15254	− 59
28	11.3	0.33	13612	15347	+351	15519	+236	15530	+217
Av.				14996		15283		15313	
Av. deviation from mean					±264		±192		±179

Apparatus—Air is displaced from the 10-liter bottle, *B*, by allowing water to flow into it by gravity from bottle *A*. The air is forced through *C*, containing a 33 per cent solution of potassium hydroxide, and through *D*, containing concentrated sulfuric acid, into the Erlenmeyer flask containing the coal and distilled water. The air is forced through the upwardly inclined condenser into *E*, which contains calcium chloride previously saturated with carbon dioxide. Tube *F* contains pumice impregnated with anhydrous copper sulfate, and topped by a layer of calcium chloride. Tube *G* contains calcium chloride and tube *H* contains soda lime with a layer of calcium chloride in the last limb of the tube. The Geissler bulb contains concentrated sulfuric acid and serves as a bubble counter.

The coal was boiled with dilute hydrochloric acid and the liberated carbon dioxide absorbed in soda lime. A 5-gram sample of 60-mesh coal was placed in a 300-cc. Erlenmeyer flask, and 75 cc. of recently boiled distilled water added. The flask was shaken to wet the sample thoroughly and then connected to the train. The air in the apparatus was displaced by bubbling carbon dioxide–free air through at the rate of 2 or 3 bubbles per second. During this period the soda-lime absorption tube, *H*, and the calcium chloride guard tube, *G*, were not connected to the apparatus. The mixture in the Erlenmeyer flask was boiled during this period to remove any adsorbed carbon dioxide. The carbon dioxide absorption tubes were then connected to the train, the dilute hydrochloric acid allowed to drop slowly into the Erlenmeyer flask, and the contents of the flask boiled. During this time a steady stream of carbon dioxide–free air was passed through the apparatus for about 30 minutes. Tube *F* absorbs any hydrogen sulfide liberated from the pyrite by the action of hydrochloric acid. The increase in weight in the carbon dioxide absorption tubes is the weight of carbon dioxide in the sample.

Table III—Calculated Unit B. t. u., Including Correction for CO_2

Seam	Condition	CO_2	Observed B. t. u.	$\frac{\text{B. t. u.} - 5000\,S}{1.00 - [1.08\,(\text{Ash} + CO_2) + 22/40\,S]}$	Diff.	$\frac{\text{B. t. u.} - 4650\,S}{1.00 - [1.08\,(\text{Ash} + CO_2) + 3/4\,S]}$	Diff.
		%					
Dorchester	Untreated	0.10	14669	15395		15416	
	Float	0.04	14830	15351		15432	
	Sink	0.90	12412	15358	44	15558	142
Blair	Untreated	0.08	14670	15285		15309	
	Float	0.04	14913	15270		15305	
	Sink	0.35	12560	15303	33	15376	71
Parsons	Untreated	0.03	13964	15187		15228	
	Float	0.07	14479	15105		15234	
	Sink	0.16	12050	15132	82	15223	11
Low Splint	Untreated	0.05	13981	14963		14997	
	Float	0.05	14339	14865		14885	
	Sink	0.30	10745	14924	98	14995	112
Taggart	Untreated	0.40	14800	15244		15258	
	Float	0.05	15037	15300		15241	
	Sink	3.23	12600	15336	92	15347	106
Lower Banner	Untreated	0.11	14589	15590		15625	
	Float	0.11	14800	15528		15546	
	Sink	0.32	12921	15575	62	15687	141
Upper Banner	Untreated	0.54	14488	15380		15394	
	Float	0.18	14882	15370		15383	
	Sink	2.42	11923	15503	133	15535	152
Jawbone	Untreated	0.67	12599	15133		15158	
	Float	0.24	14261	15036		15061	
	Sink	0.76	11911	15067	97	15099	97
Imboden	Untreated	0.15	14285	15004		15034	
	Float	0.02	14655	15025		15049	
	Sink	0.47	11702	14937	88	15021	
Merrimac	Untreated	1.41	12087	15553		15581	28
	Float	0.13	14674	15463		15488	
	Sink	1.58	11569	15551	90	15584	96
Av. of differences between lowest and highest B. t. u.					82		96

Table IV—Calculated Unit B. t. u., Including Correction for CO_2 on Coal from Merrimac Seam

Sample	CO_2	Observed B. t. u.	$\frac{\text{B. t. u.} - 5000\,S}{1.00 - [1.08\,(\text{Ash} + CO_2) + 22/40\,S]}$	Deviation from Av.	$\frac{\text{B. t. u.} - 4650\,S}{1.00 - [1.08\,(\text{Ash} + CO_2) + 3/4\,S]}$	Deviation from Av.
	%					
1	0.45	8070	15614	− 29	15637	− 36
2	0.44	13155	15622	− 21	15637	− 36
3	0.97	12735	15569	− 74	15584	− 89
4	2.60	10620	15680	+ 37	15785	+112
5	1.47	12674	15662	+ 19	15681	+ 8
6	1.91	10439	15857	+214	15989	+316
7	2.75	9681	15575	− 68	15787	+114
8	2.61	13116	15612	− 31	15636	+ 37
9	2.43	13414	15667	+ 24	15699	+ 26
10	0.81	13398	15564	− 79	15578	− 95
11	0.52	13297	15566	− 78	15579	− 94
12	5.40	11486	15844	+202	15873	+200
13	0.83	10661	15720	+ 77	15737	+ 64
14	1.06	13827	15646	+ 3	15666	− 7
15	3.44	12582	15690	+ 47	15710	+ 37
16	1.55	13713	15589	− 56	15606	+ 67
17	4.44	12643	15781	+138	15793	+120
18	0.45	14179	15507	−136	15522	−151
19	0.34	13439	15557	− 86	15570	−103
20	0.27	13207	15530	−113	15545	−128
21	2.67	12803	15675	+ 32	15695	+ 22
22	0.82	13088	15636	− 7	15647	− 26
23	3.23	12423	15772	+129	15800	+127
24	2.25	13390	15621	− 22	15635	− 38
25	0.97	13797	15480	−163	15495	−178
26	0.56	12743	15730	+ 87	15756	+ 83
27	2.25	13416	15673	+ 30	15688	+ 18
28	0.26	13612	15558	− 85	15581	− 92
Av.			15643		15673	
Av. deviation from mean				± 75		± 86

Analytical Data

Table I gives analyses of the untreated, float, and sink portions of each coal on the moisture-free basis. The unit B. t. u. calculated from the three previously mentioned formulas are given. Under the heading "Difference" is given the difference between the lowest and the highest B. t. u. value for each coal for each formula.

As a further check on the adequacy of the correction formulas, they were applied to a series of samples of coal taken from the same mine. It was assumed that different samples of coals from the same coal seam and the same mine should have practically the same elementary composition, even though the proximate analyses might show wide variations in ash, sulfur, and B. t. u. Accordingly, 28 samples of the coal (*2*) from the Merrimac seam were used.[3]

[3] These samples were obtained from the Slusser Mine and used in obtaining data for Bulletin 5 of the Engineering Experiment Station.

Table II shows the analyses of these coals on the moisture-free basis, together with the unit B. t. u. as calculated from the three formulas. The deviation in B. t. u. from the average of the calculated unit B. t. u. for each formula is given for each sample.

The fact that some of the calculated unit B. t. u. varied widely from the average suggested the presence of a disturbing factor which was not being corrected for. The coals were all analyzed for carbon dioxide and the unit B. t. u. by the Parr formula, and the Fieldner formulas were recalculated to take into consideration the presence of the carbon dioxide. Since the carbon dioxide is lost in the ash determination, it must be added to the percentage of ash. Parr's formula becomes

$$\frac{\text{B. t. u.} - 5000\,S}{1.00 - [1.08\,(\text{ash} + CO_2) + 22/40\,S]} \qquad (4)$$

and the Fieldner formula,

$$\frac{\text{B. t. u.} - 4650\ S}{1.00 - [1.08\ (\text{ash} + CO_2) + 3/4\ S]} \quad (5)$$

Tables III and IV give the carbon dioxide content of the various coals and the unit B. t. u. calculated to take this factor into account.

Discussion of Results

The unit B. t. u. values for the Virginia coals under investigation are in best agreement when calculated by the Fieldner modification of the Parr formula. However, it is necessary to correct for the carbon dioxide which is present in considerable amount in some cases.

When the carbon dioxide correction is also applied, the original Parr formula gave the better agreement.

For the 28 samples from the same mine, the unit B. t. u. calculated by the formula

$$\frac{\text{B. t. u.} - 5000\ S}{1.00 - [1.08\ (\text{ash} + CO_2) + 22/40\ S]} \quad (6)$$

gives fairly constant values, the average deviation being ±75 B. t. u. By use of the Fieldner modification of Parr's formula, the average deviation is slightly higher, ±86 B. t. u. These variations may be due to the inherent variations in the different layers of the coal seam, but neglecting this factor the average deviation is not very much greater than the experimental error in the B. t. u. determination.

Acknowledgment

The authors wish to acknowledge the assistance of A. V. Warren, research fellow in chemistry, for his help with much of the analytical work, and the advice of A. C. Fieldner of the U. S. Bureau of Mines, chairman of the American Standards Association Sectional Committee on the classification of coal, who suggested the investigation as of importance to the work of this committee.

Literature Cited

(1) Bird and Messmore, Bur. Mines, *Repts. Investigations* **2586** (1924).
(2) Fish and Addlestone, Virginia Poly. Inst. Eng. Expt. Sta., *Bull.* **5** (1929).
(3) Fieldner and Selvig, *Trans. Am. Inst. Mining Met. Eng.*, **78**, 597 (1930).
(4) Hillebrand, U. S. Geol. Survey, *Bull.* **70**, 217–19 (1919).
(5) Parr, S. W., "Analysis of Fuel, Gas, Water, and Lubricants," McGraw-Hill, 1922.
(6) Parr and Wheeler, Univ. Ill. Eng. Expt. Sta., *Bull.* **37** (1909).

Indirect Estimation of Silicon in 48 to 52 Per Cent Ferrosilicons[1]

George T. Dougherty

6833 Anthony Ave., Chicago, Ill.

A DIRECT method of determination on this class of material has always been standard, but has the serious disadvantage of being slow and time-consuming, requiring $1^1/_2$ or 2 days. Speed is commercially important and economical when it is desirable to avoid a car demurrage. Fifty per cent ferrosilicons are usually about 48 to 52 per cent silicon, iron making up the difference except 0.5 up to 2 per cent of foreign matter (C, Mn, P, S, Al, Ni, Co, Ti, Cu, Cr, etc.). The writer has developed a rapid and satisfactory method of estimating silicon by difference instead of directly. A result may be reported in about half a day or a little longer and will be very close to results obtained by the long direct method, at any rate close enough for technical purposes. It is far less difficult to check up in duplicate by the indirect than by the direct method.

Apparatus Required

A modified form of the well-known type of Hillebrand's radiator (*1*, *2*) of sheet iron or, preferably, nickel [$^1/_{32}$ inch (0.079 cm.) thick], mouth and bottom open, with a 2-inch (5.08-cm.) flange all around the outside, being welded to the bottom of the radiator. Radiator is 3 inches (7.92 cm.) in diameter at the top, $2^1/_2$ inches (6.35 cm.) at the bottom, and 2 inches (5.08 cm.) high.

A sheet-iron or nickel capsule 2 inches (5.08 cm.) in diameter at the top, $1^1/_2$ inches (3.81 cm.) at the bottom, and $1^1/_4$ inches (3.18 cm.) high. No cover.

A 35- or 50-cc. platinum or, permissibly, Palau crucible and cover.

A platinum rod 2 inches (5.08 cm.) or $2^1/_2$ inches (6.35 cm.) long, 14 or 15 gage; must be 1 inch (2.54 cm.) longer than the top diameter of the crucible.

A chromel triangle 3 inches (7.92 cm.) and $2^1/_2$ inches (6.35 cm.) between sides.

For assembling, insert the capsule partly within the 3-inch (7.92-cm.) chromel triangle inside the Hillebrand radiator and push it down to a level with the bottom of the radiator. Bend the sides or legs of triangles to wedge or fit in.

[1] Received December 29, 1930.

Next, insert the platinum crucible (when ready after treating the weighed sample with acids as directed below) partly within the $2^1/_2$-inch (6.35-cm.) chromel triangle and place it within the capsule already within the radiator, the sides of the $2^1/_2$-inch (6.35-cm.) triangle resting on top of the capsule. The platinum crucible must never be allowed to touch the bottom of the capsule, or a loss may result by spattering.

The platinum rod will cross the mouth of the crucible under the crucible cover near the cover handle or tip. This arrangement affords a vent for fumes of hydrofluoric acid and sulfur trioxide and efficiently retains any spattered matter while evaporating down.

The object of the capsule is to prevent a gas flame from coming in contact with the bottom of the platinum crucible, and to throw the heat more against the upper walls of the crucible in order to nearly equalize the temperature inside it and thus promote a quiet steady boil and evaporation. The whole apparatus constitutes an open hot-air bath and, of course, must be used under a hood.

Procedure of Indirect Analysis

The clean platinum crucible and cover and platinum rod are freshly ignited together and weighed after allowing to cool 10 or 15 minutes to recover their normal equilibrium. Weigh into the crucible exactly 0.5 gram of the 100-meshed sample (a 200-meshed sample sometimes causes a violent reaction with acids added). Pour into the crucible from a small beaker a *cooled* mixture of 36 drops (1.5 cc.) of concentrated sulfuric acid and 10 cc. of water. Next add 5 cc. of 48 per cent hydrofluoric acid from a 25-cc. graduated Bakelite cylinder (with lip and foot). Cover at once; do not use the platinum rod until directed later. Let the crucible stand in the cold for 15 minutes or so; then place it on a hot plate near the edge (on a strip of sheet asbestos if necessary) at a temperature of 80° to 90° C. for about 15 minutes. Next move it nearer the center of the hot plate at a little above the boiling

point of water (110° to 125° C.) to boil gently for about 10 minutes. A 35-cc. crucible requires more watching than a 50-cc. crucible for fear of its boiling over. At the end of the 10 minutes' boil, take off the crucible with the cover still on, and let it stand for 15 minutes on a $2^1/_2$-inch (6.35-cm.) chromel triangle on a ring stand to cool off, so that acid vapors condensed to a liquid may wash down any particle of spattered sample from the inside cover and walls of the crucible.

Set the crucible partly within the $2^1/_2$-inch (6.35-cm.) chromel triangle inside the radiator down to about 1 inch or $^1/_2$ inch above the bottom of the capsule which is already inside the radiator. Insert the platinum rod between the mouth of the crucible near its edge and the cover near its handle. Start heating with a low Méker flame whose tip barely touches the bottom of the capsule.

If, after heating 20 minutes, no white fumes of sulfur trioxide have begun to come off, raise the flame a little. When sulfur trioxide fumes finally stop evolving, turn on more gas flame gradually until in about 10 minutes the bottom of the capsule is almost red hot. Transfer the crucible, etc., to another triangle on another ring of the ring stand to cool. The cover and rod will usually be found bright and clean and free from stains. If any stains are seen, brush them back into the crucible. Now tilt the crucible with cover on (handle down) in the triangle. Lay the platinum rod aside for the time. Apply the Méker flame first on the cover handle and move the flame little by little at each time toward the bottom of the crucible, when sulfur trioxide fumes will suddenly burst out from a splitting-up of iron sulfates, and then heat the whole crucible red hot for a few minutes. Place the crucible on a clean porcelain slab or plate to cool off. The inside walls and cover of the crucible will usually show brown stains of ignited iron oxide. Brush these stains into the crucible. Set the crucible alone in the triangle and heat red hot from a new or good Méker burner for 30 minutes. Also at the same time, heat the cover and rod red hot for the length of time in another triangle. Cool for 10 minutes and weigh the crucible, cover, and rod together.

The increase of weight represents the amount of ignited residue. Multiply this by 2 and by 100 and by 0.6977 to obtain a per cent of metallic iron and all other ingredients except silicon. Subtract this product from 100.00 to find the per cent of silicon. This factor (0.6977) applies only to platinum crucibles. If a 35- or 50-cc. Palau crucible and cover were used, the factor 0.6946 must be used instead. There is an appreciable action on Palau by hydrofluoric acid, sulfuric acid, and sulfates of iron while boiling, evaporating, and igniting. This accounts for the small difference in the respective factors. Palau crucibles lose in weight considerably more than platinum crucibles do after each such analysis, but will last a large number of these analyses.

After such kind of work, platinum or Palau crucibles and covers and rods are easily cleaned by brushing off residues and boiling for 15 to 25 minutes in 250-cc. beakers with 1 to 1 hydrochloric acid more than covering the crucibles, etc.

It is wholly unnecessary, and, indeed, perilous to add any nitric acid to the mixture of sulfuric acid and hydrofluoric acid because of a violent reaction with a possible serious loss of sample. The iron in the ignited residue is wholly in a state of ferric oxide, with perhaps mere traces of ferrous oxide or possibly sulfur trioxide, any slight error from which has been absorbed in the factor applied.

This indirect method should answer just as well for 75 or 98 per cent ferrosilicons, both of which are considerably used in non-ferrous foundries.

The author obtained the factors 0.6977 and 0.6946 by running according to the above described indirect method in a platinum and a Palau crucible, a U. S. Bureau of Standards Sample No. 59, officially marked 50.00 per cent silicon and 48.4 per cent iron (leaving 1.60 per cent for impurities), with results as follows:

Weight of Ignited Residue

Gram	*Gram*
35-CC. PLATINUM CRUCIBLE	50-CC. PALAU CRUCIBLE
0.3585	0.3602
0.3581	0.3598
0.3584	0.3598
50-CC. PLATINUM CRUCIBLE	Average = 0.35993 × 2 = 0.71986
0.3585	0.5 gram silicon ÷ 0.71986 = 0.6946, factor
0.3584	
0.3580	
Average = 0.3583 × 2 = 0.7166	
0.5 gram silicon ÷ 0.7166 = 0.6977, factor	

Literature Cited

(1) Hillebrand, U. S. Geol. Survey, *Bull.* **700**, 33.
(2) Hillebrand and Lundell, "Applied Inorganic Analyses," pp. 21–3, Wiley, 1929.

A Modified Slow-Combustion Pipet[1]

Kenneth A. Kobe

School of Chemistry, University of Minnesota, Minneapolis, Minn.

THE slow-combustion method for the determination of combustible gases has many advantages over the explosion method. When it is carried out by one who uses the apparatus infrequently, it often becomes explosive. This is usually due to a too rapid admittance of gas, causing an explosive mixture to pass the heated filament, or else too slow a rate, causing an explosive mixture to form in the manifold. By the use of a vertical filament the former danger is removed.

The pipet of Steacie (*2*) is not suited to use in standard gas-analysis apparatus. A suitable modification is shown in Figure 1. Here the pipet is of the usual form (*1*) except that one contact tube has been made 2 inches (5.08 cm.) shorter than the other tube. The longer tube has a short side arm, *A*, the end of which is drawn out into a small loop through which the heating filament can pass. The heating element is lengthened to about 7 inches (17.78 cm.) and is made in the form shown. The side arm prevents the filament from inclining to either side and holds it in the center of the tube under the opening from the capillary. Now when the gas is passed in so rapidly that it passes the heated spiral, it is still in contact with a glowing wire, so that combustion takes place instead of an explosion. When the air or oxygen for the combustion is delivered to the pipet, a short thread (about a half inch, or 1.27 cm.) of the flushing liquid is left in the capillary of the pipet. This effectively separates the gas and oxygen so that no explosive mixture can form in the manifold, and a flash back cannot take place when the gas is passed into the pipet.

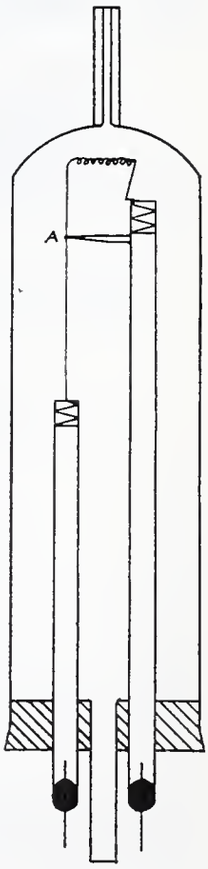


Figure 1—Diagram of Slow-Combustion Pipet

Literature Cited

(1) Carnegie Steel Co., "Methods of Chemists of United States Steel Corporation for Sampling and Analysis of Gases," pp. 14 and 31, Pittsburgh, 1927.
(2) Steacie, *J. Am. Chem. Soc.*, **52**, 2811 (1930).

[1] Received January 21, 1931.

Use of Steam for Kjeldahl Distillation of Nitrogen[1,2]

Jesse Green

Montana Agricultural Experiment Station, Bozeman, Mont.

A steam still for the nitrogen determination, as described here, has as its principal advantages freedom from bumping and greater speed in operation, with accuracy equal to the still heated by gas or electricity.

SEVERAL years ago Edmund Burke, chief chemist of the Montana Experiment Station, visited the laboratory of the New York Experiment Station and saw in operation a two-unit steam nitrogen still. It was thought that this principle might be used on a larger scale as part of the regular method for determining nitrogen, so a still with six units was designed and built. This method of distillation has been used in the Montana Experiment Station laboratories over a period of 30 years. Meanwhile the still, as Figure 1 shows, has been gradually developed into a very efficient apparatus. It now consists of a set of individual jacketed condensers, *A*, with the cooling water coming in at *C* and leaving at *D*. The steam for distillation enters the manifold at the valve *E* and any water is drained off through the trap *F*. Steam is distributed from the manifold through needle valves, *G*, which give the fine regulation and are never moved once they are adjusted. The angle valves, *H*, are used to turn the steam on and off, but are not used for regulation of the rate. Nipples are screwed into the angle valves and connected to the steam delivery tubes, *I*, by means of short pieces of rubber tubing. The steam delivery tubes extend nearly to the bottom of the distillation flasks.

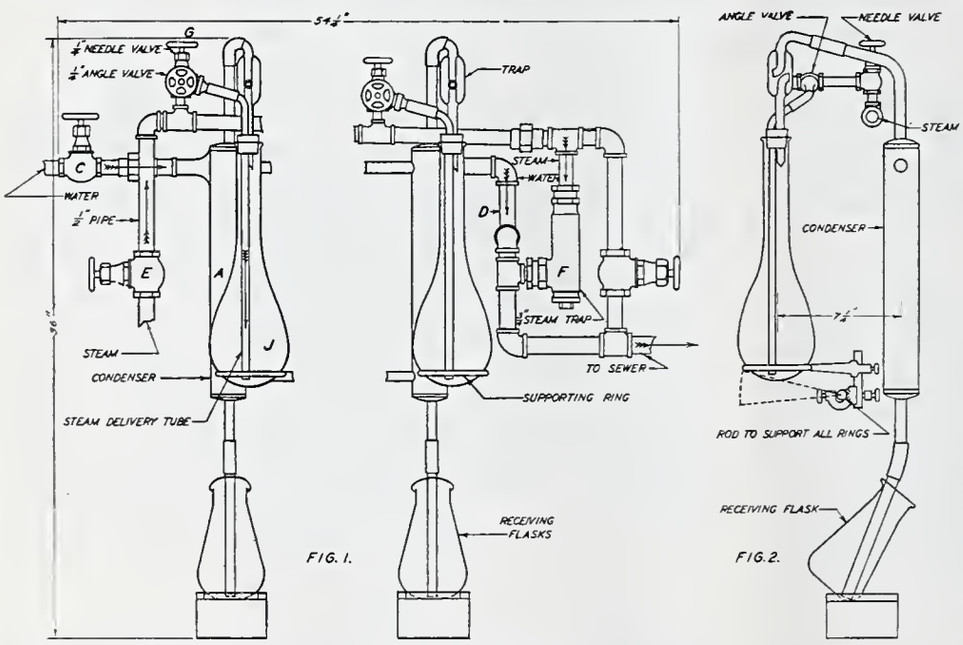


Figure 1—The Two End Units of Steam Nitrogen Still
Figure 2—Side View of Single Unit of Steam Nitrogen Still Showing Convenient Method of Placing Receiving Flask

Samples are diluted to 250 cc., made alkaline, and put on in the usual way, except that no boiling stones are necessary. The angle valves are then opened, allowing all the steam passing the needle valves to flow freely into the liquid in the distillation flasks, *J*. The steam rises through the liquid carrying the ammonia rapidly up through the traps and down through the condenser as distillate into the receiving flasks.

Figure 2 shows a single unit of the apparatus, illustrating a very advantageous way of setting the receiving flask. Some laboratories now use this method of placing the receiving flask, but it has not been generally adopted. A block with cleats nailed around three of its edges supports the flask. The glass tip is adjusted in length so that when it is put down to the corner of the flask, it will not allow the flask to stand in a vertical position when the block is placed snugly beneath. When the flask is standing in a sloping position with the tip down to the corner, the maximum depth of the tip in the acid is attained. With this arrangement, the practice of adding distilled water to raise the level of the acid is not necessary.

Steam at 30 pounds (2.11 kg.) gage pressure, or 231 cm. of mercury absolute pressure, is used to operate the still and gives good results, though other pressures would probably offer no difficulties. A standard hopper-type condenser could be used in place of the jacketed tubes that are shown.

The needle valves are adjusted so that a distillation is made in 10 minutes, and a distillate of 200 cc. is collected. The rate and efficiency of the method are shown by the data presented in the following discussion.

A 0.1 *N* ammonium sulfate solution was prepared from the salt made from pure sulfuric acid and ammonia. The method for making the material was that used in the standardization of sulfuric acid by neutralizing the ammonia and weighing the ammonium sulfate formed (*1*).

Twenty cubic centimeters of this solution were made alkaline and distilled as in the regular nitrogen determination. The titrations are given in Table I, and the results show an average recovery in six determinations of 99.90 per cent of the theoretical amount of nitrogen present.

A criticism may be made because 100 per cent was not recovered, but the difference between 99.90 per cent and 100.0 per cent in titrating a 20-cc. sample with 0.1 *N* reagent is 0.02 cc., really well within the experimental error. In taking another 200-cc. distillate from the same samples no additional nitrogen was recovered, and thus the distillation was complete in the first 200 cc.

In order to show the rate of distillation, six 20-cc. samples of 0.1 *N* ammonium sulfate were distilled for only 5 minutes, collecting 100-cc. distillates. These distillates contained 99.55 per cent of the nitrogen in the samples showing that 10 minutes are sufficient in which to make a distillation with steam. The remaining 0.45 per cent of the nitrogen was collected in a second distillation of the samples.

[1] Received November 17, 1930.

[2] Montana Agricultural Experiment Station, Paper No. 1, Journal Series.

Table I—Distillation of Standard Ammonia Solutions with Steam
(20-cc. samples of 0.1 *N* ammonium sulfate solution used)

Alkali Titration	Blank	Difference[a]	Ammonia Recovered
Cc.	*Cc.*	*Cc.*	%
FIRST DISTILLATION, 10 MINUTES			
5.45			
5.50			
5.56			
5.60			
5.51			
5.48			
Av. 5.52	25.50	19.98	99.90
CONTINUED DISTILLATION, 10 MINUTES			
5.07			
5.12			
5.12			
5.11			
5.12			
5.09			
Av. 5.11	5.11	None	None

[a] Cc. of 0.1 *N* alkali equivalent to ammonia coming over in 200 cc. of distillate.

Table II—Comparison of Electric and Steam Distillation

Sample	Nitrogen Recovered	
	Electric still, in 32 min.	Steam still, in 10 min.
	%	%
Wood	0.254	0.249
Flour	1.996	2.008
Cottonseed meal	7.021	7.044

The data given in Table II show a comparison of the work of the steam still with the regular equipment. Three samples were prepared, wood, flour, and cottonseed meal, representing typical materials of low, medium, and high nitrogen content, respectively. The same still was used and was operated first by electricity and then by steam. The percentages of nitrogen found are the average of six closely agreeing determinations made by distilling over 200 cc. of distillate. In every case with steam a second distillation was made which showed that all the nitrogen was collected in the first distillate. The results of the steam distillation practically equal the same work done with electricity.

Discussion

The greatest disadvantage of the steam still is that it must be located where steam is available. As most modern buildings are equipped with steam, this disadvantage will be of no consequence. It has the advantage of being absolutely free from bumping. Steam enters the distilling liquids causing an agitation which continues uniformly throughout the process. With soils this feature is of greatest importance.

Distillations are made with steam in 10 minutes, or one-third of the time required with electricity. Repeated tests show that this time is sufficient, although it may appear to be too short. A consideration of the action of steam in a distillation will help to explain the reason why less time is required. When steam is turned on, distillation begins almost immediately; also the agitation from the passing of the steam tends to sweep the ammonia out of the liquid in a rapid and efficient way.

The steam still requires less space than an electric still of the same capacity. It is lower in cost, a six-unit electric still costing $90, while a steam still of the same size can be constructed for $78.

The costs of installation of the two types will vary, but probably are about equal. Although no measurements were made on operation costs, it is the opinion of the writer that steam is the more economical. If the steam trap is working properly there are no losses of live steam. The ordinary radiation losses from the pipes and that used to produce 200 cc. of distillate is the amount required to make a determination.

Literature Cited

(1) Scott, "Standard Methods of Chemical Analysis," p. 504, Van Nostrand, 1920.

Notes on the Determination of Hemicelluloses[1]

R. C. Malhotra

St. Mary College, St. Marys, Kan.

An attempt has been made to standardize the conditions for the estimation of the hemicelluloses. It has been suggested that residue left after the removal of alcohol-soluble sugars and starch be put in 100 cc. of 2.5 per cent hydrochloric acid and heated for 4 hours in a pan. The pan should contain 3 liters of water and the depth should be marked and made up at the end of every hour. After hydrolysis of hemicelluloses, reduced sugars may be determined by any of the standard methods. Some possible sources of error have been explained.

Within recent years, hemicelluloses have occupied an important position as plant reserve materials. Murneek (*11*), Roberts (*14*), Clements (*3*), Roberts and Link (*15*), and other physiologists and biochemists seem to attribute many plant activities to the seasonal changes of polysaccharides, including hemicelluloses.

The writer (*8*) was engaged in determining the chemical changes which may take place in plants grown at different temperatures. During the course of these studies, a uniform and accurate procedure for the estimation of various carbohydrates was evidently needed, since the chemical differences in plants not grown at similar temperatures are at times very small, but nevertheless should be estimated. The writer could not find a detailed procedure which would yield uniform results in connection with hemicelluloses.

It is probably true that several authors, such as Murneek (*10*), Nightingale (*12*), Plimmer (*13*), Haas and Hill (*5*), and others, have mentioned the fact that after the estimation of starch, the residue contains hemicelluloses and cellulose. This fraction, when hydrolyzed for 4 hours with 2.5 per cent hydrochloric acid, yields hemicellulose sugars. However, during this procedure, no uniform system of the degree and kind of heat (even for the same duration of time), the amount of water (in case hydrolysis is carried in the steam bath), or the total volume of the acid to be used, is mentioned. Yet the writer's experiments seem to indicate that all these factors may cause a variation in the determination of hemicelluloses. The procedure mentioned in this paper seems to yield uniform and comparable results.

Experimental Method

Cabbage and lettuce plants were grown at 75° F. (22.2° C.) in the greenhouse of the University of Chicago. At the end

[1] Received January 17, 1931.

of 5 months they were cut, dried at 70° C., cooled in a desiccator, ground, and pulverized until they could pass through 60-mesh screen. About 3-gram samples (*6*) were obtained.

First, sugars were removed by alcohol extraction after the method by Browne (*2*). Starch was separated by saliva according to Gardner's (*4*) method. The residues left after

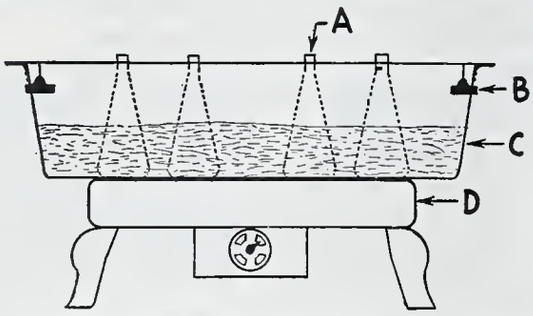


Figure 1—Arrangement of Erlenmeyer Flasks, Container, Screen, Weights, and Hot Plate, Side View

A—Erlenmeyer flask C—Pan
B—Weight D—Hot plate

filtering sugars, obtained from starch fermentation, were put into Erlenmeyer flasks containing 50, 100, and 150 cc. of 2 per cent hydrochloric acid. Several baths with different amounts of water were set up, using Central Scientific hot plate 7570, the steam bath and asbestos pad on electric hot plates.

In one case, 3 liters of water were poured into a container which was 30 cm. in diameter at the bottom and 42 cm. at the top. Flasks were placed in water after a heavy wire screen with holes was put over them to hold them in place. At the four corners of this screen, a 400-gram weight was tied as a protection against spilling or floating of the samples. The water level of the container was marked. At the end of every hour, more water was added to make up the original total. This container was satisfactory for running 8 samples at one time. The arrangement of the flasks, container, screen, and weights is shown in Figures 1 and 2.

After 4 hours of boiling, the mixture was filtered and made up to 100 cc. and the sugars were estimated by Fehling's solution following the method of the Association of Official Agricultural Chemists (*1*), titrated with potassium permanganate according to Mathews (*9*), and calculated as dextrose. The samples were run in duplicate.

Discussion of Data

The figures recorded in Table I show the quantitative yield by different procedures. It may be seen that in 50 cc. of hydrochloric acid with 3 liters in the steam bath without any additional water, the yield is not only the minimum, but the duplicates do not check very closely. Fifty cubic centimeters of hydrochloric acid do not seem to be enough to hydrolyze the residue (original sample about 3 grams). As the water of the container evaporates, it may react differently, at various surfaces, until it is about dry. One hundred cubic centimeters of hydrochloric acid seem to show better results than 50 cc.

When 50, 100, and 150 cc. of the hydrochloric acid were added, but the volume of water in the container was increased to 4.5 liters, on the whole, the yield of hemicelluloses was reduced, although in some cases the difference was very small. It is evident that the larger volume of water used for the bath in this case requires more heat. Since the amount of heat was the same in both cases, the bath with 3 liters would boil more vigorously than that of 4.5 liters. Thus the yield for the former should be more than that for the latter, as was actually the case. The figures indicate a relationship between the yield of hemicelluloses and the volume of the hydrochloric acid used.

The steam bath, with 100 cc. of hydrochloric acid, shows somewhat higher and more uniform figures than any analysis recorded in the first six columns. Steam baths seem to be satisfactory, but when this method was repeated, using a different pressure, the figures did not check. Thus, if the steam pressure used could be kept constant throughout the experiment, this procedure might be used. Since there is now no method for regulating the pressure of a steam bath it is not practicable.

Table I—Hemicelluloses in Cabbage and Lettuce on Dry Weight Basis

Plant	No Addition of HCl						100 cc. 2.5% HCl Added		
	3 liters water			4.5 liters water			Steam bath	Asbestos, no additional water	Screen, kept at 3 liters water
	50 cc.	100 cc.	150 cc.	50 cc.	100 cc.	150 cc.			
	%	%	%	%	%	%	%	%	%
Cabbage	5.87	5.93	6.10	5.53	5.80	5.98	6.04	8.51	6.41
	5.98	6.01	6.34	5.71	5.91	6.22	6.23	7.78	6.48
Lettuce	5.38	5.43	5.86	5.41	5.37	5.91	5.55	6.01	5.36
	5.47	5.62	5.68	5.53	5.49	5.72	5.67	6.31	5.32

Hydrolysis of the mixture with an asbestos pad under direct heat yielded the most variable results. This would be expected first, because all parts of the plate do not heat equally; second, because, the direct heat being stronger and the cell walls containing variable amounts of hemicelluloses (*7*), some portions may yield more than others.

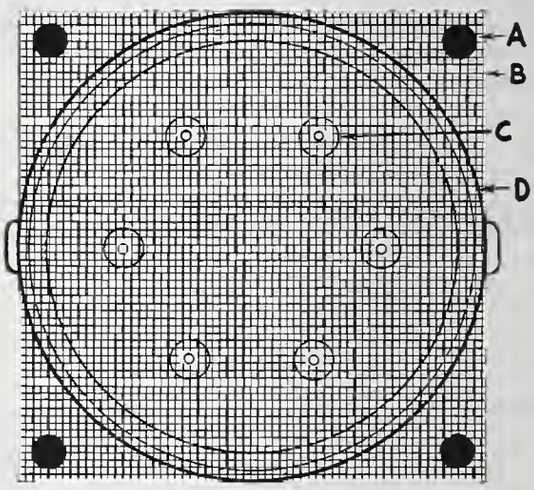


Figure 2—Same Apparatus, Top View

A—Weight C—Erlenmeyer flask
B—Screen D—Pan

The yield in the case of the 2.5 per cent hydrochloric acid solution made up every hour to a volume of 3 liters may not be the highest, but the analytical results are more uniform than with any other procedure used in this study. Since in most biochemical studies comparable results are necessary, this procedure may be desirable, as shown by these tissues. Furthermore, the data gained by these experiments may be of some use to analytical biochemists.

Acknowledgment

It is a pleasure to acknowledge the help rendered by my student Edmond J. Hogan in making the drawings used in this article.

Literature Cited

(1) Assocn. Official Agr. Chem., Methods, p. 134 (1925).
(2) Browne, "Handbook of Sugar Analysis," 1914.

(3) Clements, University of Chicago, Ph.D. Thesis, 1929.
(4) Gardner, University of California, Ph.D. Thesis, 1927; *Plant Physiol.*, , **4**, 405 (1929).
(5) Haas and Hill, "Chemistry of Plant Products," Longmans, 1929.
(6) Malhotra, Ind. Eng. Chem., Anal. Ed., **2**, 398 (1930).
(7) Malhotra, *J. Biochem. (Japan)*, **12**, 341 (1930).
(8) Malhotra, *Proc. Am. Soc. Hort. Sci.* (1930), in press.
(9) Mathews, "Physiological Chemistry," Wood, 1930.
(10) Murneek, Mo. Agr. Expt. Sta., *Res. Bull.* **119** (1928).
(11) Murneek, *Plant Physiol.*, **4**, 251 (1929).
(12) Nightingale, Wis. Agr. Expt. Sta., *Res. Bull.* **74** (1927).
(13) Plimmer, "Practical Organic and Biochemistry," p. 213, Longmans, 1920.
(14) Roberts, Wis. Agr. Expt. Sta., *Res Bull.* **68** (1926).
(15) Roberts and Link, *Proc. Am. Soc. Hort. Sci.* (1930), in press.

Portable Equipment for Crushing and Quartering Samples of Coal, Coke, or Other Lumpy Materials[1]

E. S. Pettyjohn

University of Michigan, Ann Arbor, Mich.

IN ORDER to facilitate reduction in the weight and size of the material obtained when sampling lump coal, large-sized coke, or other lumpy materials at locations other than the laboratory, a portable steel quartering hopper and a portable steel hand crusher have been designed.

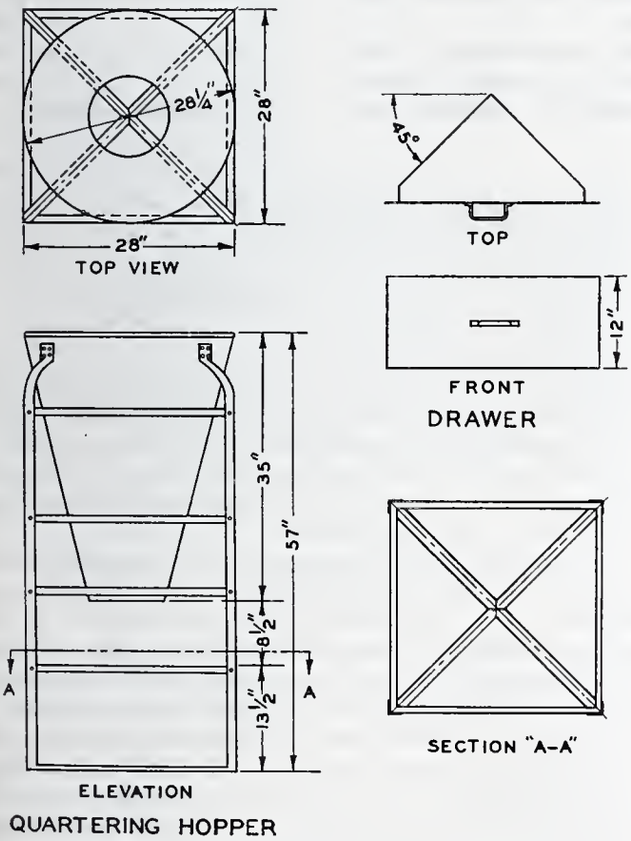


Figure 1—Apparatus for Quartering Coal Samples

The quartering hopper (Figure 1) consists of an inverted cone supported by four legs attached near the top of the cone. The inverted cone discharges onto the cross section of two steel angles which are placed directly below the cone and diagonally from the supporting legs. Below the angles and resting on the steel base are four triangular boxes of approximately $1^1/_3$ cubic feet (40 liters) capacity. The sample to be reduced in weight is introduced into the hopper and discharged onto the cross section of the steel angles which uniformly direct the falling material into the four triangular boxes. The sample is thus divided into four equal parts. The use of the quartering hopper materially increases the ease with which large samples of bulky materials may be reduced in weight.

The steel hand crusher (Figure 2) consists of a circular hopper attached to the upper side of a steel plate perforated with holes 1 inch (2.54 cm.) in diameter. The plate and hopper are supported on a rectangular base in which is located a steel drawer of approximately 2 cubic feet (60 liters) capacity. A steel-headed tamper fitted with a wooden handle is used to crush the material. The sample to be reduced in size is emptied into the circular hopper and the larger lumps are broken and forced through the holes in the perforated plate with the steel tamper. The high sides of the circular hopper prevent the material from scattering during the crushing operation. The crushed material falls into the steel drawer as it passes through the holes in the plate and is easily withdrawn and emptied into a suitable container. The use of the steel hand crusher greatly increases the ease with which lumpy material may be reduced in size, and at the same time avoids possible contamination of the sample.

It is often possible to introduce the sample directly into the quartering hopper as taken. The quartered sample is then reduced in size in the crusher and reintroduced into the hopper for further quartering. A second plate with smaller sized holes may be placed on top of the larger sized holed plate in the crusher and a further reduction in the size of the material obtained The sample may then be again introduced into the quartering hopper and a final sample obtained which will be suitable for transfer to the laboratory for final reduction and analysis.

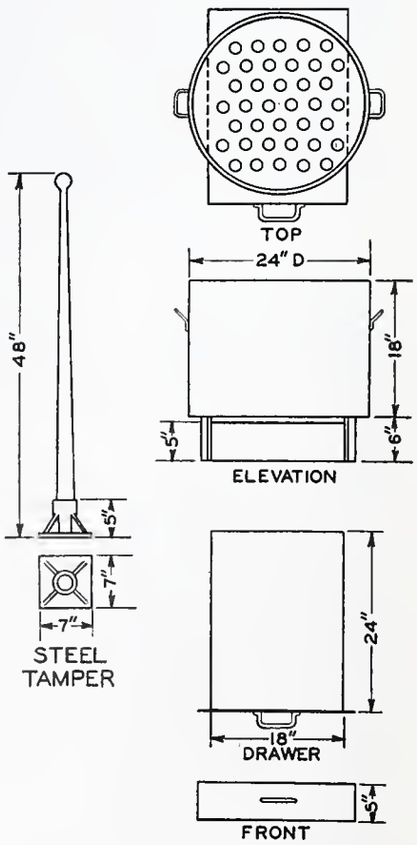


Figure 2—Apparatus for Crushing Coal Samples

The quartering hop-

[1] Received January 2, 1931.

per and hand crusher are easily constructed and are portable. The details of construction are presented in the accompanying plates. The dimensions may be modified to suit the particular material to be handled. The hopper and crusher constructed by the author were used to sample coal up to 8-inch (20-cm.) lumps.

Quantitative Determination of Calcium, Magnesium, and Phosphorus in Feedstuffs and Cattle Excreta[1,2]

Improved Technic

H. P. Morris, J. W. Nelson, and L. S. Palmer

Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minn.

A procedure for treating the ash of samples to be analyzed for minerals is described which gives decidedly higher results when the materials contain large quantities of substances insoluble in hydrochloric acid. These substances are believed to be complex silicates which are completely broken down by fusion with sodium carbonate. The platinum dishes used are not affected by the carbonate fusion.

Samples of hay and cow feces are affected most markedly by the new procedure.

Silicic acid does not affect the determination of calcium by the volumetric method, but when it is determined by the gravimetric method the silicates must be removed by dehydration.

It has been recognized for several years that considerable difficulty is encountered in quantitative mineral analyses of ash samples containing large quantities of acid-insoluble material. It has been found in this laboratory that the treatment of the ash from feedstuffs and cow excreta in many cases is an important factor in the quantitative recovery of calcium, magnesium, and phosphorus, the three minerals studied. Noticeable quantities of material insoluble in hydrochloric acid had been observed after treating such ash samples with 6 *N* hydrochloric acid. In rechecking some of these solutions for calcium it was found that longer treatment of the insoluble fraction with the acid increased the amount of calcium recovered. In 1913 Dutcher (*2*) concluded that the ash of cow feces should be boiled in concentrated hydrochloric acid for 3 hours, and the insoluble residue treated with a solution of sodium hydroxide. Dutcher's method is time-consuming, attended with danger of spattering, and gives appreciable and variable blanks, especially when silica dishes are used in the ashing process. A method has been devised in this laboratory to effect complete solution of the ash without the disadvantages mentioned.

Experimental Procedure

We will first present a detailed description of the methods which we now employ for the determination of calcium, magnesium, and phosphorus in feedstuffs and excreta. Data will then be presented showing how the results obtained by these methods compare with those secured by the older methods.

Determination of Calcium—Two grams of air-dried material to be analyzed are weighed into a platinum dish and ashed overnight at a dull red heat. The ash is then fused with from five to ten times its weight of anhydrous sodium carbonate. In the fusion step it is important that all the sodium carbonate be melted and intimately fused with the ash. After cooling, the dish containing the fused mass is placed in a 250-cc. beaker and covered with a watch glass. Sufficient distilled water is added to moisten the sample and then 10 cc. of 1 to 1 hydrochloric acid are added. When the fused material is dissolved, it is transferred quantitatively to a 100-cc. volumetric flask and made up to volume with distilled water. The sample is mixed thoroughly, and if cloudy, filtered through an acid-washed ashless filter paper (such as Schleicher and Schüll No. 589). The calcium is precipitated by a modification of the Kramer and Howland (1926) procedure (*4*), while the washing and draining is adapted from Clark and Collip's (1925) blood calcium method (*1*). A 25-cc. aliquot is pipetted out of the clear solution into a 50-cc. Pyrex centrifuge tube which tapers to a point. Ten drops of a 0.04 per cent solution of dibromo-cresol purple indicator are added followed by 10 cc. of a saturated ammonium oxalate solution. The solution is made alkaline with concentrated ammonium hydroxide and then slightly acid with 1 *N* hydrochloric acid. It is then heated on a steam bath for a few minutes, cooled, and the pH adjusted to 5.8 (dirty gray color) with dilute ammonium hydroxide and hydrochloric acid if necessary. The precipitate is allowed to stand overnight or digested on the steam bath for 2 hours. It is then made up to 40 cc. volume with distilled water and centrifuged at 1300 r. p. m. for 10 minutes.[3]

The supernatant liquid is saved for the magnesium determination by carefully decanting it off into another similar centrifuge tube. The calcium tube is inverted on a filter paper and allowed to drain for 10 minutes. After draining, any liquid remaining around the edge of the tube is wiped out with a clean dry towel. The precipitate is stirred up with a stream of dilute ammonia water from a wash bottle (2 parts of concentrated ammonia hydroxide to 98 parts of water), using 40 cc. The tubes are centrifuged again, the wash solution decanted off and discarded, and the tubes then inverted on filter paper and drained for 10 minutes. After draining, any liquid remaining around the edge of the tube is wiped out as before. The calcium oxalate precipitate is then dissolved by adding 10 cc. 1 *N* sulfuric acid and heating in a boiling water bath. The titration is carried to the first faint pink color lasting one minute with 0.01 *N* potassium permanganate.

The calculations are as follows:

$$\frac{\text{Cc. } KMnO_4 \times \text{normality} \times 20 \text{ (as 1 cc. } N\ KMnO_4 = 20 \text{ mg. Ca)} \times 4 \text{ (to correct for size of aliquot)} \times 100}{2000 \text{ (mg. sample)}} = \%\ \text{Ca}$$

Determination of Magnesium—Magnesium is precipitated as the phosphate according to the Kramer and Howland

[1] Received December 18, 1930.

[2] Published with the approval of the director as Paper 989, Journal Series, Minnesota Agricultural Experiment Station.

[3] The centrifuge used is Size 2 made by International Equipment Co., Boston, Mass. It holds six of the 50-cc. tubes.

Table I—Effect of Various Procedures upon Quantitative Recovery of Calcium, Magnesium, and Phosphorus from a 2-Gram Sample of Cow Feces

Expt.	Procedure	Calcium	Magnesium	Phosphorus
		%	%	%
1	Ashed in silica dishes, treated overnight with 6 *N* HCl	0.852 0.859	0.503 0.503	0.437 0.435
	Ashed in silica dishes, treated with cold 6 *N* HCl: 4 days	0.941 0.941		
	6 days	0.947 0.945		
3	Ashed in silica dishes, boiled for 3 hours in beaker with 6 *N* HCl using glass beads to prevent spattering; silica dish removed; excess HCl evaporated, then dehydrated with 10 cc. of 5% NaOH; residue finally dissolved in dil. HCl and filtered	0.948 0.949	0.557 0.609	0.461 0.461
	Range of blanks on treatment 3	0.25 to 0.44 mg.	0.515 to 3.62 mg.	0.16 to 0.38 mg.
	Estimated net recovery using highest blank	0.926 0.927	0.376 0.428	0.442 0.442
4	Ashed in platinum, dissolved with HF, excess HF evaporated off, residue taken up in dil. HCl	1.03 1.06	0.752 0.645	0.429 0.429
		1.03 1.05	0.841 0.685	0.441 0.437
	Range of blanks on treatment 4	0.077 to 0.596 mg.	0 to 1.41 mg.	0 to 0.18 mg.
5	Ashed in platinum, fused with 1 to 2 grams Na_2CO_3 (5–10 times wt. of ash) at white heat, dissolved in 6 *N* HCl and filtered	1.068 1.063 1.065 1.066 1.060 1.063 1.053 1.064	0.916 0.910 0.880 0.910 0.933 0.933 0.922 0.895	0.487 0.481 0.508 0.508 0.483 0.481
	Average	1.063	0.913	0.491
	Range of blank on treatment 5	Less than 0.01 mg.	To 0.06 mg.	No blank

(1926) method (*4*) and finally determined colorimetrically by use of the Fiske and Subbarow (1925) method (*3*). After obtaining the trichloroacetic acid solution of the magnesium ammonium phosphate by the Kramer and Howland method, it is filtered if cloudy and then transferred to a 100-cc. volumetric flask with distilled water. Ten cubic centimeters of Fiske-Subbarow ammonium molybdate No. I (2.5 per cent ammonium molybdate in 5 *N* sulfuric acid) and 4 cc. of the reducing reagent are added, and then the solution is treated as described for the phosphorus determination. If the magnesium content is low, a 0.5 mg. phosphorus standard is also prepared.

The calculations are as follows:

$$\frac{20 \times 1 \text{ (mg. standard)} \times 4 \text{ (for aliquot)} \times 0.7742 \text{ (to convert P to Mg)} \times 100}{\text{Reading unknown} \times 2000 \text{ (mg. sample)}} = \%\ \text{Mg}$$

Determination of Phosphorus—An aliquot of the same solution used for the calcium determination is taken which will give approximately 1 mg. phosphorus. To prevent the loss of phosphorus on ashing when the material being analyzed is low in calcium, a separate sample is weighed out and 2 cc. of a 10 per cent solution of calcium acetate are added. When calcium acetate is used, the ash is then fused and treated as described for the determination of calcium. Phosphorus is then determined colorimetrically by the Fiske and Subbarow method. The aliquot is measured out into a 100-cc. volumetric flask, diluted to about 75 cc. with water, 10 cc. of Fiske-Subbarow molybdate solution No. II (2.5 per cent ammonium molybdate in 3 *N* sulfuric acid) are added, and the sample mixed. Then 4 cc. of a 0.25 per cent solution of aminonaphtholsulfonic acid are added and the aliquot is made up to 100 cc. For the standard, 10 cc. of a dihydrogen potassium phosphate solution containing 1 mg. of phosphorus are used. Ten cubic centimeters of Fiske-Subbarow molybdate solution I and 4 cc. of the reducing reagent are added. The sample is allowed to stand for 5 minutes, then it is shaken and read in a colorimeter, matching the color of the unknown with that of the standard set at 20.

The calculations are as follows:

$$\frac{\text{(Standard set at) } 20 \times 1 \text{ (mg. standard)} \times 4 \text{ (for aliquot)} \times 100}{\text{Reading unknown} \times 2000 \text{ (mg. sample)}} = \%\ \text{P}$$

Comparison of Results with Those Obtained by Other Methods

In Table I are presented the results of various procedures upon the recovery of calcium, magnesium, and phosphorus from a sample of dried cow excreta, chiefly feces. Although the data presented in this and subsequent tables have been checked and verified by one and sometimes several similar pairs of duplicate results obtained by another independent worker, in most cases the individual analyses of only one of the two or more sets of duplicate determinations are presented. However, the data for procedure 5 are mostly replicas rather than sets of duplicate determinations. The presentation of all the data would not add to the conclusiveness of the results.

Table I shows that contact with 6 *N* hydrochloric acid for several days increases the calcium recovered. Boiling for 3 hours with the same strength acid followed by dehydration of the residue with sodium hydroxide did not yield as high a percentage of calcium, magnesium, and phosphorus when the blanks were subtracted, although the total amount recovered was somewhat higher. This procedure proved quite unsatisfactory because of the wide range in the blanks obtained. When hydrofluoric acid was used to dissolve the ash, much higher results were obtained for both calcium and magnesium. There was, however, a large and variable blank for both the calcium and the magnesium determinations. Some difficulty was also experienced in making the colorimetric determination of phosphorus. Apparently the presence of fluorine interfered with the reduction of the phosphomolybdate, although the excess acid was removed by heating on a steam bath for 1 to 2 hours. The use of the hydrofluoric acid showed that the hydrochloric acid–insoluble material was mostly silicates, since practically all of this was dissolved by the hydrofluoric acid. It was therefore decided to try a fusion

process to break up the silicates. The samples were ashed in platinum as described under treatment 5, and then the ash was fused with 5 to 10 times its weight of anhydrous sodium carbonate. It was found that no more carbonate was necessary than was required to break up the silicates. The fusion procedure gave consistent quantitative yields of all three elements and insignificant or no blanks.

Recovery of Added Mineral Elements

Table II gives data showing the recovery of known quantities of calcium, magnesium, and phosphorus added to a sample of dry cow feces before ashing and then treated as described under treatment 5 in Table I. Excellent recovery of calcium and phosphorus was obtained. The recovery of magnesium showed an error of +4.7 per cent, but considering the amount added and the error of the determination, it may be said that the recovery is within the limits of error in the determination of small quantities of magnesium.

Table II—Recovery of Known Quantities of Calcium, Magnesium, and Phosphorus Added to 2 Grams of Dry Cow Feces and Treated by Fusion Procedure

	Calcium	Magnesium	Phosphorus
	Mg.	*Mg.*	*Mg.*
Original composition of sample	21.26	18.26	9.82
Amount added	6.977	2.070	10.00
Recovered in excess of amount originally in sample	7.02	2.167	10.04
Recovery, %	100.617	104.68	100.40
Error, %	+0.617	+4.68	+0.40

Table III—Effect of Adding Crude Silicic Acid on Recovery of Calcium from Cow Feces When Treated by Fusion Procedure

Crude Silicic Acid	Total Calcium Recovered	Calcium in Crude Silicic Acid Added	Net Calcium Recovered	Net Calcium Content of Sample
Mg.	*Mg.*	*Mg.*	*Mg.*	%
0	20.80	..	20.80	1.040
25	20.71	0.25	20.46	1.023
500	22.98	2.18	20.80	1.040

Effect of Added Silicic Acid on Quantitative Recovery of Calcium

The effect of adding different amounts of crude silicic acid to a sample of cow feces is shown by data in Table III. When correction is made for the calcium present in the silicic acid used, it will be noted that large quantities of silicic acid do not affect the quantitative recovery of calcium by the volumetric procedure used in this laboratory. In fact, in our study a better recovery was secured when 500 mg. of silicic acid were added than when only 25 mg. were added. The percentage of calcium in the silicic acid was practically the same for the different amounts used. It was determined by applying the fusion method in the same manner as used for the feces sample.

Comparison of Fusion Method with Older Methods

Gravimetric Estimation of Calcium—A number of determinations have been made to test the effect of the fusion method on the recovery of calcium by the gravimetric procedure. Table IV gives some of the data obtained relative to this point. It will be observed in experiment A that essentially the same results were secured by the gravimetric method as were obtained by the volumetric method when the ash was dissolved in 6 *N* hydrochloric acid, allowed to stand overnight, then heated for a short period and filtered while hot. However, when the residue remaining on the filter paper was fused with sodium carbonate and its calcium determined volumetrically, 0.16 per cent more calcium was secured. When this calcium in the residue is added to that under A, it gives a quantitative recovery. When the ash was fused and the calcium determined by the gravimetric method, without removing the silicates, high results were obtained as shown in experiment C of Table IV. However, if the silicates were removed by a dehydration step as in experiment D, then the calcium recovered was essentially the same as obtained by the volumetric procedure without the dehydration. This shows that the presence of large amounts of silicates do not affect the precipitation of calcium when the calcium oxalate is determined by titration of the free oxalic acid with potassium permanganate. It also shows that when calcium is determined by the gravimetric procedure, the silicates must be removed by dehydration before the precipitation of the calcium as the oxalate.

Table IV—Determination of Calcium by Various Gravimetric Procedures

Expt.	Description	Calcium
		%
A	2 grams cow feces; ash dissolved in cold HCl overnight followed by heating for 15 min. and filtering while hot; calcium gravimetrically	0.92
		0.92
		0.89
		Av. 0.91
B	Residue from experiment A fused with Na_2CO_3	0.16
		0.16
	Total recovery (A + B)	1.07
C	2 grams cow feces; gravimetric method applied to fused sample	1.48
		1.48
D	2 grams cow feces; gravimetric method, sample fused with Na_2CO_3; dissolved in HCl and dehydrated to remove silicates	1.079
		1.036
		Av. 1.058

Determination of Calcium, Magnesium, and Phosphorus in Various Materials—Table V shows the results obtained by the old method of simply dissolving the ash of the sample with cold 6 *N* hydrochloric acid in comparison with the results of the new method in which the ash was fused with sodium carbonate before solution with hydrochloric

Table V—Comparison of Old Method with New Fusion Method on Various Types of Material

Sample	Av. Calcium Recovered			Av. Magnesium Recovered			Av. Phosphorus Recovered		
	Old	New	Old/New	Old	New	Old/New	Old	New	Old/New
	%	%	%	%	%	%	%	%	%
Grain mixture[a] (183)	0.070	0.072	97.22	0.091	0.097	93.81	0.242	0.244	99.18
Grain mixture (195)	0.041	0.042	97.62	0.084	0.085	98.82	0.222	0.234	94.87
Prairie hay (140)	0.303	0.549	55.19	0.137	0.238	57.56	0.057	0.068	83.82
Prairie hay (129)	0.348	0.603	57.71	0.160	0.232	68.97	0.055	0.070	78.57
Alfalfa hay (12563)	1.648	1.889	87.24	0.332	0.335	99.10	0.231	0.260	88.84
Alfalfa hay (12670)	1.506	1.639	91.89	0.438	0.438	100.0	0.128	0.145	88.28
Timothy hay (12431)	0.204	0.284	71.83	0.086	0.114	75.44	0.101	0.136	74.26
Timothy hay (12430)	0.215	0.287	74.91	0.086	0.107	80.37	0.095	0.125	76.00
Green cow feces (230)	0.045	0.149	30.20	0.009	0.077	11.69	0.020	0.033	60.61
Green cow feces (231)	0.068	0.136	50.00	0.017	0.074	22.97	0.020	0.030	66.67

[a] The grain mixture was composed of 400 parts corn gluten meal, 200 parts corn, and 100 parts oats.

acid. It will be observed that grain mixtures are not influenced by the fusion method. This was to be expected since the grains do not contain any appreciable amount of hydrochloric acid–insoluble material. Timothy, prairie, and alfalfa hays show marked increase in the recovery of mineral constituents after fusion with sodium carbonate. The increase was least with alfalfa hay which ordinarily gives an ash almost completely soluble in 6 *N* hydrochloric acid. A direct comparison of the percentage recovery by the old method is shown in Table V when it is assumed that the fusion method gives a recovery of 100 per cent. All samples of forage and feces which have been reanalyzed by the new fusion method have given without exception some increase in either calcium, magnesium, or phosphorus, or of all three elements.

Literature Cited

(1) Clark, E. P., and Collip, J. B., *J. Biol. Chem.*, **63**, 461–4 (1925).
(2) Dutcher, R. A., J. Ind. Eng. Chem., **5**, 37–8 (1913).
(3) Fiske, C. H., and Subbarow, Y., *J. Biol. Chem.*, **66**, 375–400 (1925).
(4) Kramer, B., and Howland, J., *Ibid.*, **68**, 711–21 (1926).

Use of Buffers in Determination of Color by Means of Titanium Trichloride—II[1,2]

O. L. Evenson and R. H. Nagel

Food and Drug Administration, U. S. Department of Agriculture, Washington, D. C.

This paper presents work done since a previous report on this subject. Suitable buffer salts have been determined for all the titratable food colors. It has been found possible to use either sodium citrate or sodium bitartrate in all cases. Other buffer salts which may be used with each dye are also given.

In the original method for the evaluation of color in azo dyes by Knecht and Hibbert (*4*), a hot-water solution of the dye was reduced by standard titanium trichloride solution in the presence of hydrochloric acid, Rochelle salts, or sodium bitartrate. It has since been found that various other buffers, or catalyst buffers, may be used.

In a previous paper (*3*), the buffers used in determining amaranth, Ponceau 3R, and orange I were discussed. This paper is a continuation of the former report and, with the exception of erythrosin, deals with the remainder of the water-soluble coal-tar food colors which are on the permitted list issued by the United States Department of Agriculture. The percentage of pure coal-tar color in erythrosin is determined gravimetrically, hence it is not included in this report. Our present object is the same as in the preceding investigation—that is, to determine which buffers are the most suitable to use with each dye.

Materials

The dyes used were samples of certified, commercial food colors. The buffer salts, as well as all other reagents used, were of U.S.P. or c.p. quality. The titanium trichloride solution was made up in two different concentrations, 0.1 *N* and 0.05 *N*, and standardized. The hydrogen-ion determinations given were made with the quinhydrone electrode, a Leeds and Northrup type K potentiometer and a Leeds and Northrup reflecting galvanometer.

Procedure

The titanium trichloride solutions were standardized against a ferric sulfate solution made from Bureau of Standards ingot iron, and also checked against a solution of potassium permanganate which had been standardized against sodium oxalate. For the triphenylmethane dyes, the buffer salt was dissolved in 200 cc. of water and heated to boiling. It was then cooled to 85° C. under carbon dioxide gas, and 1 gram of dye, dissolved in 100 cc. of water, was added. Titration was performed at 60–70° C. For the other dyes, the buffer salt, in the quantity to be used, was dissolved in water and heated to boiling in a wide-mouthed 500-cc. Erlenmeyer flask. The dye solution was then added from a pipet and the mixture again brought to a boil. The amount of water used was such that the total volume in the flask was approximately 100 cc. when titration was begun. The dye solution was then titrated while hot under an atmosphere of carbon dioxide, and agitated by means of a mechanical stirrer. The titanium trichloride solution was added at such a speed as would permit it to react with the dye, care being taken not to add it too rapidly near the end point. Especially in the case of tartrazine, it is necessary to allow sufficient time for the reduction to take place and to keep the solution hot during the titration.

The quantity of buffer used could be varied from 10 to 20 grams without affecting the results, except in the case of the triphenylmethane dyes, where 30 grams were always used. In the experiments recorded in the tables, 15-gram portions were generally used, except in the cases noted above.

The exact method of standardizing the titanium trichloride solution and the titration procedure in detail, as well as the other methods of determining analytical data incorporated in this paper, are given in a United States Department of Agriculture bulletin (*1*).

Results

In Table I a summary is given of the results of many titrations on each of the dyes, using, or attempting to use, each of the various buffers shown. Additional data on orange I, Ponceau 3R, and amaranth are included. The numbers in parenthesis, following the name of each dye, are those given in the 1924 edition of the Colour Index. Where no number is given, the identity of the dye may be determined by consulting the Department of Agriculture bulletin and its supplement (*1*).

As in the previous paper, the color by difference has been chosen as the basis for judging the value of the results obtained with different buffers. The color by difference, in turn, is based upon a chemical analysis to determine the

[1] Received November 25, 1930. Presented before the Division of Dye Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] Seventh contribution from the Color Certification Laboratory, Food and Drug Administration, U. S. Department of Agriculture.

Table I—Titrations of Dyes with Various Buffers[c]

Dye	Sodium Citrate	Sodium Bitartrate	Rochelle Salt	Potassium Antimony Tartrate	Sodium Tartrate	Sodium Tetraborate	Sodium Bicarbonate	Calcium Gluconate	pH of Dye Soln., 1%
pH of buffer (satd. soln.)	7.63	3.42	6.73	3.66	6.52	9.15	7.75	6.76	
Amaranth (184)	(a)			(b)			(b)		5.5
Orange I (150)	(b)	(a)	(a)		(a)		(b)	(b)	7.0
Ponceau 3R (80)	(a)						(b)		7.0
Sunset yellow FCF	(a)					(b)	(b)	(b)	7.0
Ponceau SX	(b)	(a)	(a)		(a)	(b)	(b)	(b)	6.5
Tartrazine (640)	(b)	(a)	(a)		(a)	(b)		(b)	6.0
Naphthol yellow S (10)		(a)	(a)		(a)		(b)		6.0
Indigotine (1180)		(a)	(a)		(a)			(b)	4.7
Brilliant blue FCF		(a)	(a)		(a)				6.0
Fast green FCF		(a)	(a)		(a)				6.0
Light green SF yellowish (670)		(a)	(a)		(a)				3.4
Guinea green B		(a)	(a)		(a)				3.4

[a] Best results.
[b] Can be used with satisfactory results, but is not as desirable. In some cases a precipitate forms, but does not interfere with the end point.
[c] The buffers, calcium acetate, calcium carbonate, and sodium acetate, for which no results are shown, gave promising results in some cases but were not considered entirely suitable.

Note—The pH measurements of the dye solutions must be considered only approximate, in that they varied quite widely from dye to dye with the exception of light green SF yellowish, Guinea green B, and indigotine. The values for these dyes were more constant and show them to be quite acidic.

uncolored portion of a dye, consisting in general of moisture, inorganic salts, insoluble matter, and ether extractives. A large number of routine analyses have shown that, within the limit of error of analysis, this figure also agrees with the figure for total color, as calculated from the theoretical percentages of sodium, nitrogen, and sulfur present. Besides the correct color content, a buffer should also give consistent results under varying conditions, such as amount of buffer and amount of dye. The sharpness of the end point should also be considered. In general, the tartrates give a sharp end point and a clear solution, but for some dyes, as shown in the previous paper (*3*), they do not give constant results under varying conditions nor correct values (based on color by difference). Other buffers, while they give correct results and a sharp end point, form a precipitate in the titration flask and, considered from this standpoint, are not as desirable.

The triphenylmethane dyes (brilliant blue FCF, light green SF yellowish, Guinea green B, and fast green FCF) form a peculiar class, in that it has not been found possible to titrate them and obtain concordant results, except in the presence of a tartrate.

Orange I, Ponceau SX, and tartrazine may be titrated, using either sodium bitartrate, sodium tartrate, Rochelle salt, or sodium citrate as buffers. The tartrates give a slightly sharper end point than the citrate. In some samples of orange I, it is noticeable that a clear end point is not obtained. This is not due to the buffer but to an impure sample of orange I.

Since the publication of the former paper of this series, some disagreement with our results on the use of sodium bicarbonate as a buffer for orange I has come to our attention. This has been further investigated and it was found that some samples of orange I contain a trace of a subsidiary dye which causes low results and also an unsatisfactory end point, even when sodium bitartrate is used as a buffer. This subsidiary product was removed in the following manner:

One-tenth gram of orange I was dissolved in 50 cc. of water and acidified with 1 cc. of concentrated hydrochloric acid. This solution was extracted in six separatory funnels in succession, each containing 50 cc. of a mixture of equal parts of petroluem ether and amyl alcohol. All the orange I was removed from the aqueous solution in this way, leaving the red subsidiary color. The solvent was then washed with two 50-cc. portions of 0.25 *N* hydrochloric acid, which removed any remaining subsidiary color. The identity of this color has not yet been established. A pure sample of orange I, containing none of this subsidiary product, will give the same percentage color with sodium bicarbonate as with sodium bitartrate buffers, and such an orange I was used in reporting the results obtained in the former paper.

In Table II the results of complete analyses on several dyes are given. This table shows the close agreement between the color by difference and the color determined by titration when a suitable buffer is used. Similar results for amaranth, Ponceau 3R, and orange I were given in the previous paper. Analytical results on Guinea green B, light green SF yellowish, and brilliant blue FCF are not included, as the percentage of color obtained by titration differs considerably from the color by difference. This is due to an undetermined impurity known under the general term of "organic matter not dye."

As shown in Table II, a higher color content is obtained for sunset yellow FCF when using sodium citrate than when sodium bitartrate is used. This difference, although slight, is definite and has been established by a large number of titrations. It has also been noted, in our routine work of color certification, that in the case of sunset yellow the percentage of color obtained when using sodium bitartrate is always lower than the color obtained by using sodium citrate.

Tartrazine, naphthol yellow S, and Ponceau SX gave equally good results with either sodium bitartrate or sodium citrate.

Table II—Complete Analysis

	Sunset Yellow FCF	Tartrazine (640)	Naphthol Yellow S (10)	Ponceau SX	Fast Green FCF	Indigotine
	%	%	%	%	%	%
Moisture	5.62	4.3	6.4	10.4	5.0	6.6
Water insoluble	0.03	0.13	0.10	0.11	0.17	0.32
Total ether extractives	0.08	0.10	0.01	0.09	0.11	0.12
Sodium chloride	0.84	2.16	2.20	0.12	2.94	1.83
Sodium sulfate	....	.....	.....	0.43	1.45	0.42
Total not color	6.57	6.69	8.71	11.15	9.67	9.29
Color by difference (100%—total not color)	93.43	93.31	91.29	88.85	90.33	90.71
Color by titration using sodium citrate	92.4	92.0	91.4	88.8	.....	....
Color by titration using sodium bitartrate	91.2	92.3	91.4	88.8	90.1	89.5

It is rather difficult to form a theory that will explain the different behaviors of these dyes when titrated with various buffers. The word "buffer" suggests a regulation of the hydrogen ion. However, this is only one of the functions of the buffer salt in this case and is probably a minor one. For example, in the case of tartrazine, titration can be made in the presence of sodium bitartrate solution with a pH of 3.42, and equally well in a borax solution with a pH of 9.15. This shows that, if the function of the buffer is to regulate the hydrogen-ion concentration, a wide variation is allowable. On the other hand, a dye, for example, brilliant blue FCF, will titrate in the presence of Rochelle salt with a pH of 6.73

and not with sodium citrate with a pH of 7.63, a difference of less than one pH unit. From this it would seem that it is the function of the buffer to hold the hydrogen-ion concentration within certain rather wide limits, and more particularly to act in the nature of a catalyst to promote a rapid reaction between the reducing solution and the dye. A specific effect of a similar nature was also noted by Calcott and English (*2*). The buffer must also be of such a nature that it will not react with the titanium trichloride solution.

Conclusion

In the evaluation of color in a dye by means of titanium trichloride, it is essential that the correct buffer be chosen for the individual dye. The function of the buffer (or buffer catalyst) is not only to regulate the hydrogen-ion concentration, but also to promote the reduction of the dye. It has been found that in the case of sunset yellow FCF, sodium citrate gives more nearly correct results than sodium bitartrate. There are several buffers given that may be used with each dye. This is of value in titrating mixtures of dyes, as it makes possible the choice, in most cases, of a buffer that is satisfactory for them all.

Literature Cited

(1) Ambler, J. A., Clarke, W. F., Evenson, O. L., and Wales, H., U. S. Department of Agriculture, *Dept. Bull.* **1390** (revised 1927), and Suppl. 1 (March, 1930).
(2) Calcott, W. S., and English, F. L., Ind. Eng. Chem., **15**, 1042 (1923).
(3) Evenson, O. L., and McCutchen, D. T., *Ibid.*, **20**, 860 (1928).
(4) Knecht, E., and Hibbert, E., "New Reduction Methods in Volumetric Analysis," Longmans, 1918.

Determination of Hydrogen-Ion Concentration with Photoelectric Colorimeter[1]

Ralph H. Müller and Herman M. Partridge

Washington Square College, New York University, New York, N. Y.

By means of a simple photoelectric colorimeter greater precision has been obtained than by the ordinary procedure of visual estimation.

Operation of the colorimeter depends upon the variation in photoelectric current with the transmittancy of the indicator solution with changing pH value. The feeble photoelectric current is amplified by a three-electrode vacuum tube of suitable mutual conductance, and pH values are read in terms of plate current of the triode.

In a previous communication (*2*) the authors have described the use of the photoelectric cell in the performance of automatic titrations. It was shown that the change of color occurring during a titration can be followed by the photoelectric cell and, further, that the amplified output of a photoelectric cell can be made to interrupt the addition of the titrating agent at any desired end point. It was pointed out that with certain modifications this arrangement of photoelectric cell and thermionic amplifier can be used for the accurate colorimetric determination of hydrogen-ion concentration.

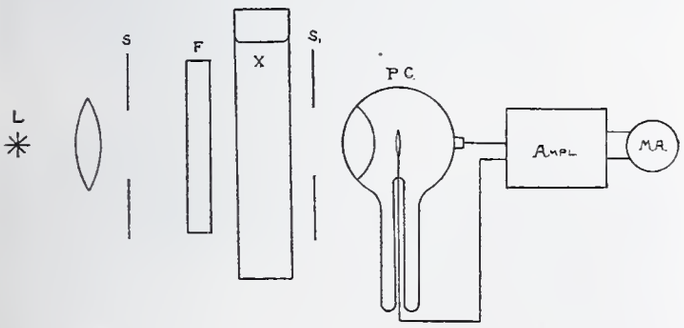


Figure 1—Scheme of Principal Features of Method

It is the object of this paper to describe the photoelectric method in detail and to show its general applicability to colorimetric procedure.

Figure 1 shows schematically the principal features of the method. Light from the lamp *L* passes through a slit, *S*, and filter, *F*, after which it traverses the solution to be investigated, *X*. The light transmitted by the latter passes through the slit *S*, and falls on the photoelectric cell, *P.C.* The amplified photoelectric current is read on a milliammeter. With linear amplification the reading of the milliammeter depends only upon the transmittancy of the solution for the particular spectral region admitted by the filter, *F*. For each particular system investigated, a filter was chosen which transmitted light of wave length corresponding to one absorption maximum of the solution.

Experimental Details

In describing the method in detail, it will be necessary to discuss very briefly the characteristics of the amplifier circuit, because certain optimum conditions have been found in the development of the method. Figure 2 shows the circuit employed, when using batteries as the source of current. The normal plate current of the vacuum tube, indicated by the milliammeter, *MA.*, depends only upon the plate voltage supplied by *B*, and the filament voltage, *A*. The grid

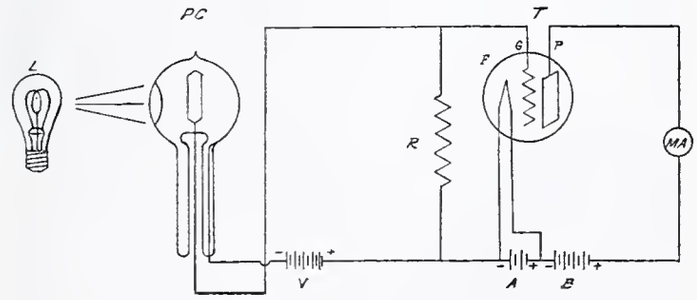


Figure 2—Amplifier Circuit Employed

potential is constant, and during operation the voltages are held constant. Any change of potential of the grid, *G*, with respect to the filament, *F*, will cause a change in the plate current. The change in plate current due to a change in grid potential—i. e., the mutual conductance of the tube—is the

[1] Received January 22, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

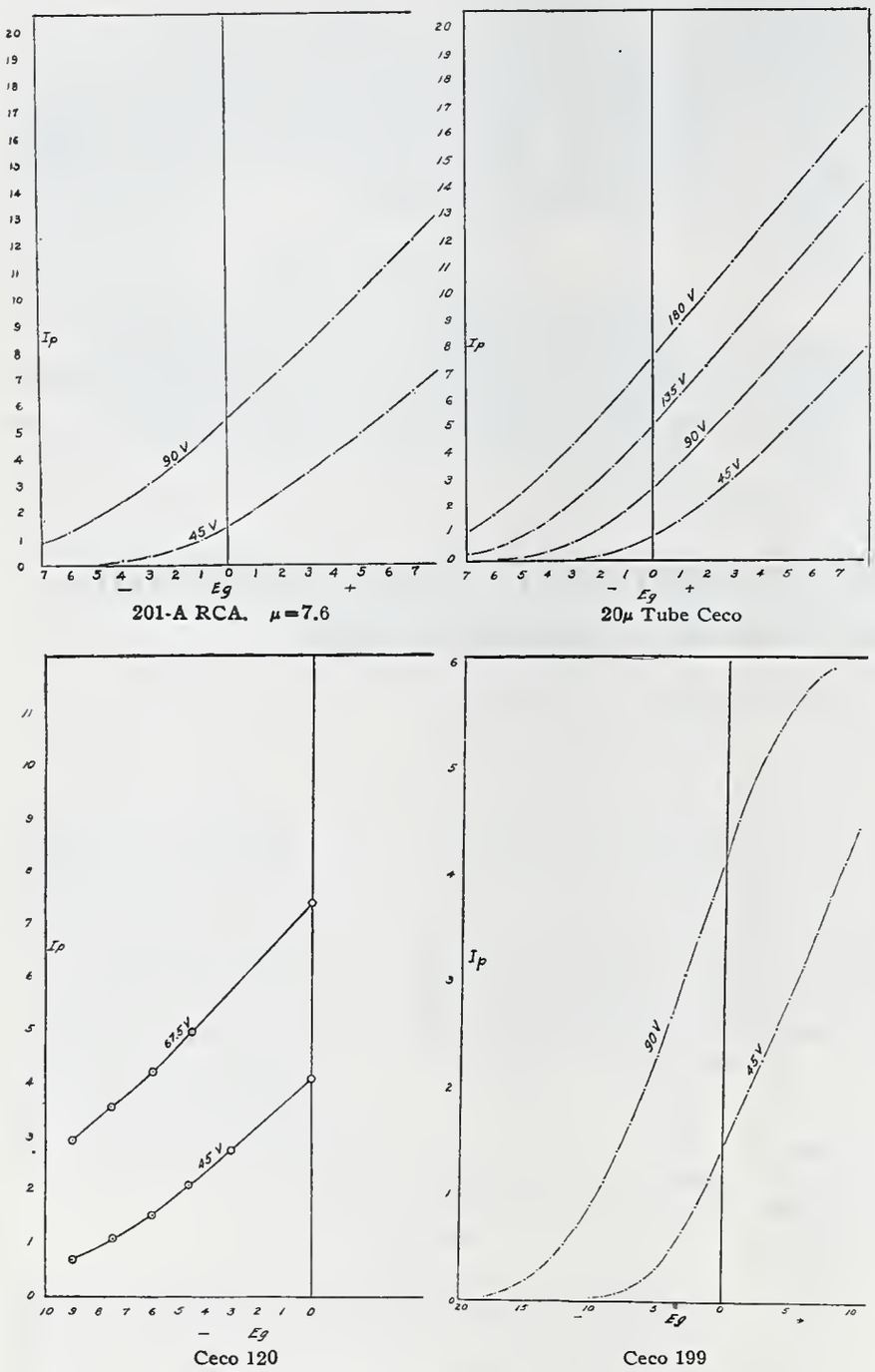


Figure 3—*Ip–Eg* Curves for Several Types of Tubes

tube constant in which we are most interested in this case. It will be seen from the diagram that changes in the grid potential are caused by the photoelectric cell in the following manner: When light falls on the active surface of the photoelectric cell, electrons are emitted, proportional in number to the intensity of the incident light, which flow through the high resistance, R, owing to the applied potential, V. The Ri drop across R is applied directly to the grid and filament of the vacuum tube. For uniform amplification it is essential that the mutual conductance of the tube be constant over the working range. That is, the relation between Ip and Eg must be linear over that range which is employed in the measurement. A further requirement is that this linear relation must obtain with negative grid potentials. Figure 3 illustrates characteristics for several types of tubes. Only the 199- and 120-type tubes are satisfactory, because the linear portion of the characteristic is on the positive side for the other types for plate potentials of less than 100 volts. The second requirement is important because positive values for the grid potential cause a flow of current between filament and grid so that the resistance of the grid circuit becomes finite and hence is less sensitive to changes due to the photoelectric cell.

If a 120-type tube is employed, B should be 90 volts, A, 3 volts, V, 135 volts, and the resistance, R, should be 5 megohms. The measurements given below were made with a sensitive millivoltmeter in the plate circuit, properly shunted so as to read milliamperes. By changing the value of the shunt the range of the instrument could be increased. This is a useful arrangement since it may happen that the system to be investigated absorbs light in a spectral region where the sensitivity of the photoelectric cell is low (in the red or orange), and therefore it becomes imperative to measure slight changes in the plate current.

Theoretical Considerations

Considerable work has been done on the absorption spectra of indicators and the dependence of absorption on the hydrogen-ion concentration. Most important in this respect is the work of Brode (*1*), in which it was shown that, contrary to the findings of many, there is no shift in wave length of the absorption maximum with change of hydrogen-ion concentration, but merely a change in the height of absorption band—i. e., change in transmittancy. In a two-color indicator there are two absorption bands, one for each color of the indicator. In the transition from one color to another, with a change of pH, the one band decreases in height as the other band increases. Brode gives accurate spectrophotometric data for most of the Clark and Lubs indicators at values covering the entire pH range. He shows that a knowledge of the transmittancy for a given wave length enables one to find immediately the pH value by referring to the pH-transmittancy curve for that indicator.

The authors have based their work on these findings and shown that if light corresponding to the maximum of absorption of the indicator is passed through a solution of the indicator and allowed to fall on the photoelectric cell, the amplified photoelectric current will depend only upon the pH of the indicator solution, other things being held constant.

Results

The data for the curves of Figure 4 were obtained in the following manner: For each indicator studied, the absorption maximum was obtained from the data of Brode. A filter was then selected which transmitted light in this region. The Wratten filters were found to be very convenient for this purpose. Each filter was checked roughly with a small spectroscope and compared with one absorption band of the indicator. It should be pointed out that it is quite impossible to obtain a filter exactly suited to each case, but since the pH–plate current values are all purely empirical relations, this makes little difference. With the filter in place, tubes containing the same amount of indicator but buffered to various pH values were placed in front of the photoelectric cell and the plate current read. A curve was then plotted with the arbitrary plate-current values as ordinates and the corresponding pH values as abscissas. The plate-current values are reduced to comparable values for the reason that the current obtained depends upon the spectral region which is being used, as mentioned above.

The curves so obtained represent a calibration curve for each indicator. By treating an unknown solution with the same amount of indicator, keeping all the other factors the same, the pH value can be obtained by comparing the plate current with the calibration curve. It should be emphasized that this procedure may be dispensed with by simply adjusting the intensity of the lamp, vacuum-tube filament, etc., to the same value at each measurement, and multiplying the observed plate current by the factor representing the ratio between pH and current for that indicator. This is permissible because the curves are all linear (over the useful range of the indicator). By the use of simple shunts and switches it is possible to use one millivoltmeter to check all voltages before a determination.

While reasonable reproducibility can be expected from the amplifier and photoelectric cell, a chemist would probably prefer to check an unknown reading in most cases by reference to a system of known pH. To do this, it is simply necessary to introduce buffered solutions containing the same indicator of several pH values above and below the unknown value, and by interpolation assure himself that the value for the unknown is not in error because of a change in tube characteristic or a variation in sensitivity of the photoelectric cell. It should be emphasized, however, that such checks need only be made occasionally, for great constancy was obtained even over long periods of operation.

It is obvious that with slight modifications in procedure, it is possible to extend the method to most colorimetric problems.

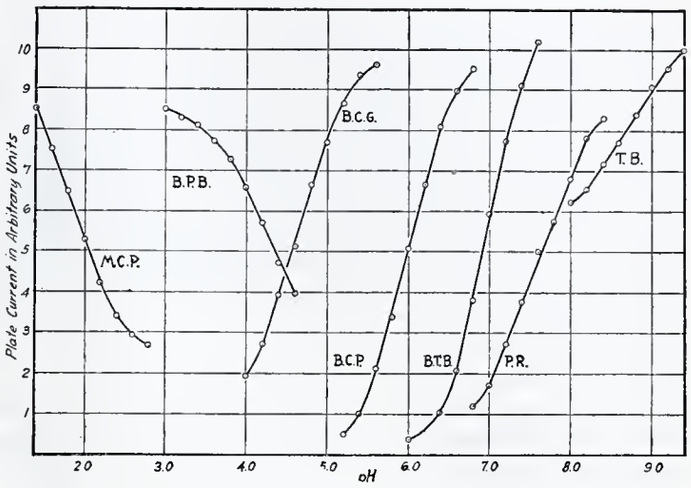


Figure 4—Calibration Curves for Various Indicators

M.C.P.—*m*-Cresol purple
B.P.B.—Bromophenol blue
B.C.G.—Bromocresol green
B.C.P.—Bromocresol purple
B.T.B.—Bromothymol blue
P.R.—Phenol red
T.B.—Thymol blue

It has been employed in this laboratory to follow color changes occurring during chemical reactions, and in this way substitute accurate values for the heretofore qualitative estimation.

Literature Cited

(1) Brode, *J. Am. Chem. Soc.*, **46**, 581 (1924).
(2) Müller and Partridge, Ind. Eng. Chem., **20**, 423 (1928).

Measurement of Rate of Formation of Oxidative Decomposition Products in Fats and Oils[1]

D. P. Grettie and R. C. Newton

Swift & Co., Union Stock Yards, Chicago, Ill.

THE intense research which is being applied to shortening material by both the producer and the user has emphasized the need of better methods for testing its various functional qualities. The susceptibility of fat to oxidative rancidity is one of the most important factors in evaluating a shortening for many uses. There is, therefore, need of a quick reliable method for determining the relative susceptibility of various fats to rancidity.

Such a method should give quickly an accurate indication of the stability of a fat under ordinary conditions. Any method in which rancidity is developed rapidly requires the application of rigorous conditions, hence it is to be expected that any such method will not give absolute comparisons of different kinds of fats for all conditions. It is possible, however, that such a method may give reliable comparisons of samples of fat from the same general source, and some indication of the relative keeping qualities of samples from different sources, if the method provides an accurate means of measuring the rancidity developed.

Several accelerated rancidity tests have been proposed. The best known of these are: (1) the oxygen absorption method, (2) the Bailey method, and (3) incubation followed by organoleptic inspection.

The oxygen absorption test (*2*) has received considerable attention, and much weight has been attached to the induction period of a fat under this test as a criterion of its keeping qualities. There is no reason to assume that the induction period for oxygen absorption is always the same as the induction period for the formation of volatile oxidative decomposition products. Since it is the volatile decomposition product which renders a fat unusable, a proper test for keeping qualities of the fat should be based upon a direct measurement of these products. For example, semi-drying oils consume large amounts of oxygen in the formation of gums, and condensation products with very little formation of the undesirable odor of rancidity.

The Bailey method (*1*) makes use of Schiff's reagent to measure the amount of volatile aldehydes produced under controlled conditions. The objection to this method lies in the fact that the Schiff's reagent, in which the volatile products of rancidity are condensed, is very unstable and difficult to maintain in a colorless condition. There is some difficulty also in measuring accurately the amount of color developed.

Probably the simplest and most reliable method heretofore developed is the incubation test in which the fat is kept in an oven at an elevated temperature and inspected for odor and flavor at regular intervals. In this test rancidity usually develops at some time between 2 and 40 days, depending upon the stability of the particular sample under test. There are, however, two objections to this method for ordinary use: the time required to get results is entirely too long for many practical purposes; and the criterion is that of odor and taste, and therefore subject to a very decided personal element of possible error in judging the point of inception of rancidity.

The Kreis test (*4*) may be used as an auxiliary indication of

[1] Received January 2, 1931.

the amount of rancidity developed at various stages of the incubation period. The Kreis test fails completely, however, when fats from different sources are compared.

The method herein described was designed to measure the relative rate of formation of volatile oxidative decomposition products of fats held under a specified set of conditions. It is a modification of the methods of Bailey and of Issoglio. Since all of the volatile products probably contribute to the odor given off by a rancid fat, the measurement of these products should be also a measurement of the degree of spoilage of the fat in question. This is performed by titrating, against acid permanganate, the products carried away in a given time interval by a constant stream of air passing over the fat which is dispersed on filter paper and maintained at a specified elevated temperature. The stream of air is drawn over the fat and then through a standard solution of acid permanganate, which is maintained at a temperature of 25° C. to condense any decomposition product picked up from the fat. This solution is then titrated against oxalic acid to determine how much has been used by the decomposition products condensed in it. The titration of the distillation products of rancid fats with permanganate was formerly proposed by Issoglio (*3*).

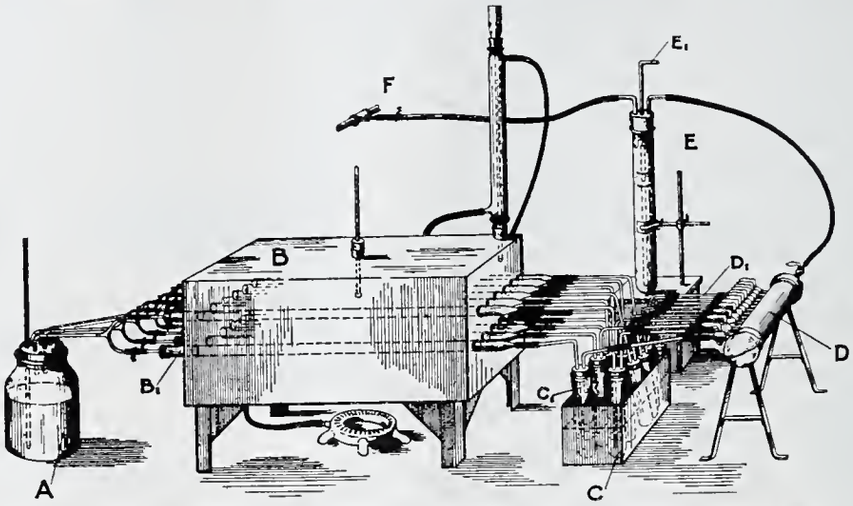


Figure 1—Apparatus for Measurement of Volatile Oxidation Products of Fats and Oils

Description of Apparatus

In Figure 1, *A* represents the wash bottle containing acid permanganate solution through which the air is drawn before passing over the fat. This washing operation is for the purpose of removing from the air any impurities which might catalyze the oxidation of the fat. Individual tubes lead from this wash bottle to the glass tubes, B_1, where they are connected by tight-fitting rubber stoppers. Means must be provided in these connections for closing off any tube not in use, or one temporarily open for the replacement of condensation tubes.

The tubular oven, *B*, is a metal box $19^1/_2 \times 14 \times 8$ inches ($49.53 \times 35.56 \times 20.32$ cm.) with two openings in the top and containing a number of tubular holes extending full length from end to end. These tubes are also made of metal and soldered water-tight throughout. The openings in the top are to accommodate a thermometer and reflux condenser. The oven is filled with water and kept at boiling temperature throughout the test. B_1 is a glass tube containing a pleated filter paper upon which the weighed fat is dispersed. This tube is 20 mm. inside diameter, except for a few centimeters at one end where it has been constricted to a diameter of about 4 mm. so that it may be connected to the glass tube, C_1, by rubber connection. This tube B_1 extends entirely through the metal tubular oven, and the filter paper is so placed that it is near the center of the oven.

The water bath, *C*, maintains equalized temperature of permanganate solution in the condensation tube. A temperature of 25° to 30° C. has been found satisfactory for this bath. C_1 is a large test tube (diameter, 1 inch, or 2.54 cm.) containing 10 cc. of 0.01 *N* potassium permanganate solution made acid with 1 cc. of approximately 5 *N* sulfuric acid. Air is allowed to bubble through this solution after passing over the fat, so that any volatile material picked up from the fat is condensed in this tube.

D is a manifolding device consisting of a 2-inch (5.08-cm.) iron pipe inset with a number of openings connected with petcocks. This device serves the purpose of connecting a number of test samples with precisely the same vacuum. D_1 is a capillary glass tube which throttles the flow of air and thereby allows a very accurate control of the volume of air passing over any test sample. This tube is connected to the manifolding vacuum device and the condensation tube. By using capillaries of the same bore and the same length, it is a relatively simple matter to obtain the same volume of air over each of a number of samples. A capillary tube of 0.5 mm. bore and 10 cm. in length gives satisfactory results.

E is a device for maintaining constant vacuum. The depth of the tube E_1 (which is open to the air) below the surface of water controls the pressure difference between the manifolding device and the atmosphere. We have regulated this depth to 29.5 cm. which, when we deduct for the total of the 13.5-cm. column in the wash bottle and condensation tube, is just sufficient to produce a flow of 1 cc. per second of air in our apparatus.

F is a vacuum line with a screw clamp for regulating the flow of air so that the incoming air at E_1 is steady and not too vigorous.

Procedure

The tube B_1 is removed and properly cleaned with acid dichromate solution, and then thoroughly dried. A piece of filter paper 5×30 cm. is creased three times lengthwise to form pleats of four layers. This paper is placed across a clean watch glass on a balance, and 2 grams of the sample of fat weighed onto it. The fat should be distributed so that when melted it will be soaked up by the entire paper. The paper is then very carefully placed in the glass tube B_1 about 8 inches (20.32 cm.) from the end, and thence into the oven, which is maintained at 100° C.

The condensing tube containing 10 cc. of 0.01 *N* potassium permanganate solution to which has been added 1 cc. of dilute sulfuric acid, is set into the water bath, *C*, and connected with the system. When all connections are adjusted, the stream of air (1 cc. per second) is started through the tube by opening the screw clamp leading to the vacuum line. At the end of 20 minutes, the condensing tube C_1 is replaced by a similar one and the contents of the first titrated as follows:

Eleven cubic centimeters of 0.01 *N* oxalic acid are added and the tube heated in a boiling-water bath until completely decolorized. This solution is then titrated with standard permanganate solution while still hot, until a faint pink appears. These replacements and titrations are made at regular 20-minute intervals until the rate of decomposition in the fat is sufficient to use up 1 cc. of the 0.01 *N* permanga-

nate solution in one 20-minute period. For samples of exceptional stability, the replacements are made hourly and the measure taken is the time required to produce a rate of decomposition equal to 1 cc. of 0.01 N permanganate solution per hour.

The above amounts were taken arbitrarily after it was found, by inspecting a large number of samples, that the odor of rancidity developed at about this point. Results are given in Table I.

Table I—Amount of Permanganate Solution Reduced between Various Time Intervals
(Duplicate determinations of sample of fat)

Sample	20 min.	40 min.	60 min.	80 min.	100 min.	120 min.	140 min.	160 min.	180 min.	200 min.
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
A	0.0	0.1	0.3	0.3	1.2	1.6				
	0.1	0.1	0.3	0.6	1.1	1.5				
B	0.2	0.2	0.2	0.2	0.3	0.5	0.5	0.6	0.8	1.4
(Oil)	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.6	0.9	1.5
C[a]	0.6	0.3	0.3	0.8	1.8					
	0.9	0.3	0.5	1.2	2.0					
D[b]	0.6	0.4	1.2							
	0.7	0.6	1.3							
	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	9 hrs.	10 hrs.
E	0.0	0.1	0.0	0.1	0.2	0.6	0.9	1.5		
	0.2	0.1	0.1	0.1	0.2	0.4	0.9	1.6		
F	0.2	0.1	0.1	0.0	0.3	0.4	0.5	1.2	2.0	
	0.3	0.0	0.1	0.0	0.2	0.5	0.9	1.1	1.8	

[a] A highly flavored fat.
[b] A very unstable fat.

Precautions

Owing to the extreme rapidity with which samples of fat are forced to become rancid under this test, there are some variables which need very careful control in order to assure accurate results.

(1) Cleaning of reaction tubes is important. The reaction tube which contains the fat dispersed on filter paper, accumulates, during the course of a test, small quantities of rancid fat closely absorbed to its surface. If this trace of fat is not completely removed it accelerates the course of rancidity of the next succeeding sample to such an extent that results are not at all reliable. These tubes can be cleaned sufficiently to give reproducible results, however, by filling and allowing to stand overnight with strong acid bichromate cleaning solution. The last trace of cleaning solution must be removed completely with distilled water.

(2) The filter paper has such intimate contact with the fat over a relatively large surface that the slightest trace of impurity leads to inaccurate results. It is necessary, therefore, to crease several sheets of filter paper at one time and discard the outside ones which have come in contact with the fingers. The type of filter paper used should be the same at all times, and should be the purest grade obtainable. It is important that extreme care be used to prevent contamination in handling the paper after it is creased while weighing the sample of fat and inserting the paper in the reaction tube.

(3) The rate of flow of air over the sample of fat has two opposite effects on the rate of the development of rancidity. It furnishes agitation of the air which keeps uniform concentration of oxygen at the reacting interface. This also carries away a portion of the volatile oxidation products which are known to have an accelerating effect on the course of rancidity if not removed. Both of these factors may be standardized, however, by fixing the rate of flow of air and also the contact of this flowing air with the surface of the filter paper. It has been found that if two of the folds in the creased filter paper become adhered at one end, or the flat surface of the filter paper is pressed against the glass so that the air does not have free circulation around all sides of the filter paper, the results will not check.

(4) There is a very slight reduction in pressure in the reaction tube owing to the column of permanganate solution through which the air is washed. All of the air must be washed through the same bottle so that there will be no difference in the air furnished the various tubes. For this reason it is essential to have a pinch clamp between the permanganate wash bottle and the reaction tube, so that any tube may be shut off while it is temporarily disconnected or out of use. If it is not shut off when disconnected, the air will be drawn through this tube in the reverse direction and then through the other reaction tubes, thus contaminating them all.

(5) It is necessary to regulate the flow of air through the reaction tubes for reasons previously mentioned. If the diameter of the capillary tube and the difference in pressure are known, the length of the capillary can then be calculated to give any desired rate of flow by Poiseuille's formula,

$$L = \frac{\pi r^4 t}{8\,NV}$$

in which L is length of capillary tube, V is the volume of air, N is the viscosity of air (0.000184), r is the radius of capillary tube, t, the time in seconds, and π the pressure in millimeters of mercury. The pressure difference can be obtained by measuring the column of water in the pressure-regulating device, and deducting that in the wash bottle and condensation tube. This can be regulated to any desired amount.

(6) It sometimes happens that water is vaporized from the permanganate condensing tubes and recondenses in the capillary tubes, thus temporarily closing them. When this happens, the air will cease to bubble through the condensation tube so that it is readily noted. In this case the capillary tube should be removed and washed out with alcohol. If it has been stopped only a few minutes, there will be no noticeable difference in the result.

Literature Cited

(1) Bailey, H. S., and Ebert, H. C., *Cotton Oil Press*, **7**, No. 8, 35 (1923).
(2) Greenbank, G. R., and Holm, G. E., Ind. Eng. Chem., **17**, 625 (1925).
(3) Issoglio, G., *Ann. chim. applicata*, **1916**, 1–18.
(4) Kerr, R., J. Ind. Eng. Chem., **10**, 471 (1918).

Dust May Replace Oil as Source of Power—Demonstrations that dust from grain elevators, factories, threshing machines, and similar sources can be used as fuel in furnaces and motors have shown the availability of a fuel which can replace oil to a large extent if the supply of that product nears exhaustion, according to David J. Price, in charge of the Chemical Engineering Division, Department of Agriculture. It is very probable that if there is another great war dust will come into extensive use as fuel, Mr. Price said. It provides a possible fuel for airplanes and automobiles, and the supply is practically limitless. Such dust is removed from the largest elevators at the rate of several carloads a day. Large supplies of it are produced from grain threshing machines, and many kinds of factories are prolific sources; tobacco factories have only recently been found to produce explosive dusts.

It has been shown that coal dust is a very economical form of fuel, and this has come into wide use.

Tests in the Department of Agriculture have proved that motors can be run on such dust. In addition, a German inventor has employed dusts in running Diesel engines successfully.

Vacuum cleaning systems are used in some plants to eliminate the dust explosion hazard. This makes the dust easily available for use as fuel. Starch, sugar, and grain dust are among those suitable for this use.

Hydrogen-Ion Concentration and the Color of Lead Chromate Pigments[1]

R. C. Ernst, E. Pragoff, Jr., and E. E. Litkenhous

University of Louisville, Louisville, Ky.

The hydrogen-ion concentration in lead acetate solutions is determined by potentiometric methods. The saturated calomel electrode is used as the standard half-cell with the quinhydrone electrode as the indicator electrode. The method is applied to the measurement of hydrogen-ion concentrations of lead acetate solutions in the preparation of lead chromate pigments. It is shown that the hydrogen-ion concentration is one of the determining factors in the colors of the resulting pigments and can be used to regulate these colors. A comparison is made of the colors obtained at the different hydrogen-ion concentrations at various temperatures, concentrations, and times of precipitation.

LEAD chromate pigments are prepared by the addition of sodium or potassium chromates or dichromates to a solution of a soluble lead salt. The colors of the resulting chromate pigments are regulated by the addition of an acid or base before precipitation to control the acidity of the lead solution. Considerable difficulty has been experienced in determining the acidity of lead solutions. The resulting colors have therefore been difficult to reproduce.

Determination of pH in Lead Acetate Solutions

The literature reveals no electrochemical method for the determination of the hydrogen-ion concentration in lead solutions. Several methods have been suggested for the analysis of lead solutions. Langnecker's (*5*) direct titration method gives a measure of the hydroxyl radical, Kolthoff's (*4*) sodium sulfate method determines the total lead and acidity. Bergh's (*1*) oxalic acid method gives only the total lead. The Fresenius and Cohn (*3*) sulfuric acid method gives the total lead and acidity. A colorimetric method by Westberg (*7*) gives, indirectly, a method for acidity of lead solutions. But none of these methods give any measure of the hydrogen-ion concentration of lead solutions.

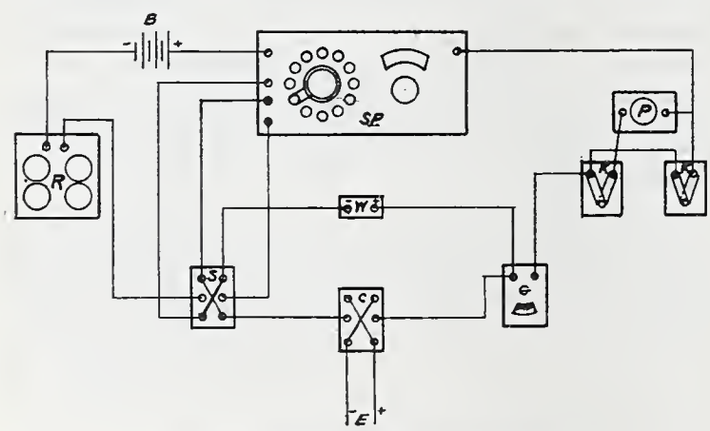


Figure 1—Diagram of Potentiometer

B—Dry cell battery
R—Resistance box
S—D.P.D.T. switch
C—Reversing switch
SP—Student potentiometer
K—Tapping keys
G—D'Arsonval galvanometer
P—Protecting resistance
W—Weston standard cell
E—To electrodes

The hydrogen-ion concentration of the lead acetate solutions was determined by measuring the electromotive force of a cell consisting of the solution with the saturated calomel electrode as a half-cell and the quinhydrone electrode of Bülmann (*2*) as the indicator electrode. The relation between the measured electromotive force and the pH (according to Sörensen, *6*) is

$$E = 0.4526 - 0.0591 \log \text{pH at } 25^\circ \text{ C.} \quad (1)$$

The electromotive force was determined by the use of the potentiometer using the circuit as shown in Figure 1. The quinhydrone electrode was used because preliminary investigation showed that the hydrogen electrode would give inaccurate results in solutions containing lead, while the quinhydrone was satisfactory below a pH of 9.

The changes in the hydrogen-ion concentration of lead acetate solutions was determined by carrying out the neutralization of an acid by a base in the presence of lead acetate. The hydrogen-ion concentration of the solution was varied by the use of 0.1 normal solutions of acetic, nitric, hydrochloric, and sulfuric acids, and potassium hydroxide. Potentiometer readings of electromotive force were taken after stirring the solutions and allowing the readings to become constant in each case. The quinhydrone electrode used dipped directly into the solution during a titration. The calomel electrode was connected to the solution by means of a salt bridge (potassium chloride and agar-agar) which prevented diffusion of potassium chloride into the lead solution.

Results of the titrations of the acids and base alone and of the acids, base, and lead acetate are shown in Table I.

These results show that acids and bases can be titrated with the quinhydrone electrode and that a maximum inflection occurs at the neutralization point. In the case of the neutralization of the acid with the base in the presence of the lead salt, the inflection also occurs at the neutralization point.

Effect of pH on Color of Lead Chromate Pigments

The effect of the hydrogen-ion concentration on the color of lead chromate pigments was determined by precipitation of the lead chromate from solutions having different hydrogen-ion concentrations.

In these experiments 0.5 normal solutions of both lead acetate and potassium dichromate were used.

The lead chromates were prepared by treating 300 cc. of 0.5 *N* lead acetate with acid and base (potassium hydroxide) until the potentiometer read the voltage corresponding to the required pH, and this solution was precipitated using 300 cc. of 0.5 *N* potassium dichromate solution. Agitation was used throughout. All precipitations were performed in 34 ± 2 seconds. The temperature was 25 ± 2° C. The value for the potentiometer reading with the corresponding pH is given. The pH's of the dichromate solutions, corresponding to the value for the electromotive force read, are probably not true pH values. All values above a pH of 9 are doubtful. The colors were determined by rubbing the pigments in clear varnish, the mass tones by rubbing the pigments in

[1] Received September 19, 1930. Presented before the Division of Paint and Varnish Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Table I—Titrations Using Quinhydrone—Saturated Calomel Electrode at 25° ± 2° C.
(Distilled water used, 100 cc.; samples used, 10 cc. of 0.1 *N* solutions)

KOH Added	Acetic Acid			Acetic Acid and Lead Acetate			Hydrochloric Acid			Hydrochloric Acid and Lead Acetate			Nitric Acid			Nitric Acid and Lead Acetate			Sulfuric Acid			Sulfuric Acid and Lead Acetate		
	E	pH	*E/C*	*E*	pH	*E/C*	*E*	pH	*E/C*	*E*	pH	*E/C*	*E*	pH	*E/C*	*E*	pH	*E/C*	*E*	pH	*E/C*	*E*	pH	*E/C*
Cc.																								
0.0	−252.7	3.40		−192.5	4.40		−314.7	2.38		−262.8	3.24		−319.0	2.30		−270.0	3.12		−326.2	2.16		−252.8	3.41	
1.0	227.0	3.93	25.7	188.0	4.44	4.5	322.0	2.24	2.7	−243.0	3.71	19.8	323.0	2.23	4.0	248.8	3.49	31.2	325.0	2.20	1.2	227.2	3.83	35.6
2.0	211.2	4.05	15.8	182.9	4.57	5.0	320.0	2.28	2.0	228.0	3.82	15.0	321.5	2.25	1.5	233.6	3.64	15.2	322.0	2.24	3.0	210.3	4.12	16.9
3.0	198.6	4.31	12.8	177.8	4.66	5.2	318.2	2.32	1.8	213.5	4.08	14.5	320.0	2.28	1.5	220.5	3.94	13.1	318.8	2.31	3.2	198.2	4.32	12.1
4.0	187.7	4.44	10.9	171.8	4.76	6.0	316.1	2.36	2.1	202.6	4.24	10.9	316.4	2.35	3.6	208.2	4.15	12.3	314.3	2.38	4.5	187.8	4.49	11.4
5.0	177.8	4.66	9.9	165.5	4.87	6.3	312.2	2.40	3.9	192.5	4.40	10.1	312.8	2.40	3.6	197.2	4.34	11.0	308.4	2.45	5.9	177.7	4.66	10.1
6.0	167.8	4.82	10.0	159.3	5.01	8.8	308.2	2.46	4.0	181.2	4.59	11.3	308.4	2.48	4.4	186.3	4.51	10.9	302.5	2.57	5.9	167.6	4.83	10.1
7.0	157.3	5.05	10.5	150.5	5.16	10.3	300.2	2.60	8.0	170.6	4.76	10.6	302.0	2.58	6.4	175.7	4.69	10.6	293.6	2.73	8.9	156.3	5.06	11.3
8.0	144.4	5.25	12.9	140.2	5.33	15.8	289.0	2.80	11.2	156.2	5.06	14.4	292.2	2.74	9.8	163.7	4.90	12.0	280.0	2.94	13.6	143.4	5.38	12.9
9.0	124.6	5.58	19.8	124.4	5.59	21.0	265.5	3.19	23.5	138.1	5.36	28.1	275.8	3.03	16.4	145.6	5.19	18.1	260.3	3.28	19.7	122.1	5.72	21.3
9.5	105.8	5.91	37.6	113.9	5.78	26.5	217.5	4.05	96.0	122.5	5.63	33.2	258.4	3.31	34.8	133.8	5.46	23.6	233.0	3.74	54.6	104.2	5.93	35.8
9.7	93.2	6.14	63.0	107.5	5.88	32.0	164.6	4.89	64.5	115.3	5.73	36.0	227.1	3.91	156.5	127.6	5.53	31.0	203.2	4.21	149.0	92.7	6.14	57.5
9.8	84.7	6.25	85.0	103.8	5.96	37.0	123.4	5.62	312.0	111.0	5.83	43.0	200.0	4.30	271.0	123.7	5.61	39.0	179.3	4.63	239.0	85.5	6.25	72.0
9.9	69.1	6.52	156.0	99.9	6.02	39.0	71.2	6.46	522.0	106.3	5.89	47.0	153.0	5.12	470.0	119.2	5.69	45.0	148.5	5.19	308.0	76.7	6.40	88.0
10.0	−33.3	7.12	258.0	95.5	6.08	44.0	−13.6	7.47	576.0	100.6	5.99	57.0	−97.7	6.04	553.0	114.4	5.76	48.0	−110.4	5.84	381.0	64.8	6.59	119.0
10.1	+30.0	8.20	633.0[a]	89.6	6.19	59.0[a]	+44.1	8.43	577.0[a]	94.6	6.10	60.0[a]	27.5	8.14	1252.0[a]	109.0	5.86	54.0[a]	+42.0	8.42	1524.0[a]	51.8	6.81	130.0[a]
10.2	67.0	8.80	370.0	86.5	6.23	31.0	65.6	8.71	215.0	91.0	6.17	36.0	55.6	8.62	281.0	105.5	5.91	35.0	70.0	8.86	280.0	43.2	6.95	86.0
10.3	86.0	9.12	190.0	83.9	6.27	26.0	82.5	9.06	169.0	88.0	6.22	30.0	80.3	9.03	247.0	102.6	5.95	29.0	79.0	9.01	90.0	35.3	7.09	79.0
10.5	105.5	9.48	77.5	79.2	6.34	23.5	96.0	9.30	67.5	83.8	6.30	21.0	108.5	9.51	141.0	97.2	6.04	27.0	91.4	9.22	62.0	−18.5	7.48	74.0
11.0	126.1	9.80	41.2	63.7	6.60	21.0	118.2	9.66	24.4	73.4	6.45	20.8	136.2	9.96	55.0	84.5	6.26	25.4	115.7	9.62	48.6	+6.5	7.79	50.0
12.0	+157.5	10.30	21.4	−46.4	6.89	17.3	+140.2	10.10	22.0	60.0	6.67	13.4	168.9	10.47	32.7	66.0	6.58	18.5	+136.0	9.96	20.3	+38.5	8.30	32.1

[a] Maximum values of *E/C* are at neutralization point of acid and base.
Note—Values above a pH of 9.0 are doubtful but are given as corresponding to obtained voltages.

raw linseed oil, and all tints and strengths by mulling 2 × 50 strokes, 50 mg. of color, 1 gram of zinc oxide, and 12 drops of linseed oil. The results of these experiments are given in Tables II to X, inclusive.

Table II—Effect of Variation of Acetic Acid and Potassium Hydroxide on H-Ion Concentration of Lead Acetate Solution
(Potassium dichromate added to the lead acetate solution)

Sample	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
1	3.5	−245.0	2.5	−305.0	3.95
2	4.0	215.0	2.5	305.0	4.25
3	5.0	157.0	2.5	305.0	4.45
4	6.0	98.0	2.5	305.0	4.55
5	6.5	67.0	2.5	305.0	4.80
6	7.0	− 40.0	2.5	305.0	5.08
7	8.0	+ 20.0	2.5	305.0	7.30
8	9.0	80.0	2.5	305.0	10.75
9	10.0	+140.0	2.5	305.0	11.30

The color of the pigments changes from a light yellow at a pH of 3 to a bright orange at a pH of 9, where a maximum brilliance and darkness of shade are obtained. Above a pH of 9 a lighter brownish offshade appears. The masstones of samples 1, 2, 3, and 4 were light clean-looking chromate yellows, sample 1 not quite so clean-looking as 2, 3, or 4. Sample 5 was a trifle dirty; 6, a little red; 7, a light orange; 8, orange; and 9, a dirty brown. Samples 2, 3, and 4 were very strong yellows, 1 was a trifle weak, 5 was weak and dirty, and 6 was a trace weaker and redder than 2 to 4. Sample 7 had a good reddish tint and strength, 8 had a purple tint, and 9 was very weak.

Table III—Effect of Variation of Acetic Acid and Potassium Hydroxide on H-Ion Concentration of Potassium Dichromate Solution
(Lead acetate added to the potassium dichromate solution)

Sample	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
10	6.5	− 67.0	2.5	−305.0	4.40
11	6.5	67.0	3.0	275.0	4.52
12	6.5	67.0	4.0	214.0	4.58
13	6.5	67.0	5.0	157.0	4.75
14	6.5	67.0	5.5	127.0	4.90
15	6.5	67.0	6.0	98.0	5.04
16	6.5	67.0	6.5	67.0	5.10
17	6.5	− 67.0	7.0	− 40.0	5.20
18	6.5	67.0	8.0	+ 20.0	5.75
19	6.5	67.0	9.0	80.0	5.98
20	6.5	− 67.0	10.0	+140.0	6.10

When the pH of the dichromate solution is changed rather than the lead acetate solution, the resulting colors change from a light yellow at a pH of 2.5 to an orange at a pH of 9. Above a pH 9 of a lighter offshade brownish yellow is formed. The masstones of samples 11, 12, 13, and 14 are a little more yellow than that of 2, 3, or 4, or else 2, 3, and 4 are a little greener. Sample 15 is a little deeper in shade and a trace dirty. Samples 16 and 17 are about as 2 and 3, 18 and 19 are a dirty brown and offshade, and 20 is almost as bad. Samples 11, 12, and 13 are as strong as 1, 2, or 3 but a deeper red tint, and 14, 15, 16 are a trace weaker. Sample 17 is the same strength as 2, 3, or 4; and 18, 19, and 20 are very weak, 19 being best.

Table IV—Effect of Variation of Acetic Acid and Potassium Hydroxide on H-Ion Concentration of Solutions Containing Precipitated Color
(Potassium dichromate added to the lead acetate solution)

Sample	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
21	6.5	− 67.0	2.5	−305.0	4.0
22	6.5	67.0	2.5	305.0	5.0
23	6.5	67.0	2.5	305.0	6.0
24	6.5	67.0	2.5	305.0	7.0
25	6.5	67.0	2.5	305.0	8.0
26	6.5	67.0	2.5	305.0	9.0
27	6.5	67.0	2.5	305.0	10.0
28	6.5	67.0	2.5	305.0	11.0

If the pH of the solution containing the precipitated color is varied with acetic acid and potassium hydroxide after precipitation, the color changes from a light yellow at a pH of 4 to a brilliant orange at a pH of 9. Above 9 an offshade color appears which is lighter than the shade of the pigment of a pH of 9. In masstone, sample 21 is slightly green and dirty, 22 is a good yellow shade, 23 is dirty, 24 and 25 are badly offshade, 26 and 28 a fair orange, and 27 is brown. Sample 21 is a little yellow in tint, of good strength, and a little dirty. Sample 22 is best. Sample 23 is reddish, 24 and 25 are weak, 26 and 28 are of fair strength with reddish tints, and 27 is a trace weaker than either 26 or 28.

Table V—Effect of Variation of Hydrochloric Acid and Potassium Hydroxide on H-Ion Concentration of Lead Acetate Solution
(Potassium dichromate added to the lead acetate solution)

Sample	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
29	3.0	−270.0	2.5	−305.0	2.80
30	4.0	215.0	2.5	305.0	4.25
31	5.0	157.0	2.5	305.0	4.45
32	6.0	98.0	2.5	305.0	4.55

The color of these pigments is a brilliant yellow. A slight change of shade in darkness is noticed in the masstones. Sample 29 is brightest and 32 is darkest, 32 showing a reddish tint. Samples 29, 30, and 31 are similar to 11, 12, and 13. Sample 29 is not quite so strong as 11 and the tint is the same. Samples 30, 31, and 32 gradually decrease in strength and the tint turns a slight purple. Sample 32 is quite weak.

Table VI—Effect of Variation of Nitric Acid and Potassium Hydroxide on H-Ion Concentration of Lead Acetate
(Potassium dichromate added to the lead acetate solution)

Sample	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
33	3.0	−270.0	2.5	−305.0	2.70
34	4.0	215.0	2.5	305.0	4.15
35	5.0	157.0	2.5	305.0	4.45
36	6.0	98.0	2.5	305.0	4.55

The colors were similar to those of 1, 2, 3, and 4, and the masstone similar to 1, 2, 3, and 4. The strength and tints were like 11, 12, and 13. Sample 34 is weakest.

Table VII—Effect of Variation of Sulfuric Acid and Potassium Hydroxide on H-Ion Concentration of Lead Acetate Solution
(Potassium dichromate added to the lead acetate solution)

Sample	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
37	3.0	−270.0	2.5	−305.0	2.75
38	4.0	215.0	2.5	305.0	4.18
39	5.0	157.0	2.5	305.0	4.45
40	6.0	98.0	2.5	305.0	4.55

The colors were similar to those of 1, 2, 3, and 4. Sample 39 is the only good color for masstone. Sample 38 is dirty and green, and 37 is dirty and red, while 39 is of fair strength and yellow tint, 38 is weaker, and 37 has no tinting strength at all.

Table VIII—Effect of Variation of Temperature of Lead Acetate and Potassium Dichromate
(Potassium dichromate added to the lead acetate solution)

Temperature	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
° C.					
25	6.5	−67.0	2.5	−305.0	4.80
40	6.5	67.0	2.5	305.0	4.45
60	6.5	67.0	2.5	305.0	4.35
80	6.5	67.0	2.5	305.0	4.20
100	6.5	67.0	2.5	305.0	3.00

At 25° C., the color is light yellow and at 80° C., a maximum darkness is obtained. Above 80° C., the color lightens and has a reddish hue. At 40° C., the masstone is dirty; at 60° C., a fair yellow; at 80° C., offshade greenish color; and at 100° C., very light orange. The tints at 40° C. and at 60° C. are the same, and both have good strength and a reddish tinge. The color at 80° C. is weak and dirty, and at 100° C., slightly orange.

Table IX—Effect of Change of Time of Precipitation of Lead Chromate
(Potassium dichromate added to the lead acetate solution)

Time	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
Min.					
33 sec.	6.5	−67.0	2.5	−305.0	4.80
15	6.5	67.0	2.5	305.0	4.80
30	6.5	67.0	2.5	305.0	4.80
45	6.5	67.0	2.5	305.0	4.80
60	6.5	67.0	2.5	305.0	4.80

No appreciable change in color was noticed in the pigments. The tints and strengths were close to those of sample 5 with the 45-minute color a trifle weak.

Table X—Effect of Variation of Concentration of Lead Acetate and Potassium Dichromate
(Potassium dichromate added to the lead acetate solution)

Normality	Lead Acetate		Potassium Dichromate		Final pH
	pH	*E*	pH	*E*	
0.5	6.5	− 67.0	2.5	−305.0	4.80
1.0	6.5	67.0	2.5	−305.0	4.80

The color, masstone, and strength of these colors are identical with sample 5.

Conclusions

Using the quinhydrone electrode to determine the hydrogen-ion concentration in the lead acetate and potassium dichromate solutions, lead chromates were precipitated. The acidity was regulated by means of acetic, hydrochloric, nitric, and sulfuric acids. In each case the color changed from a yellow at a pH of about 3.5 to an orange at a pH of 9, which was a maximum. Above a pH of 9 the colors became offshades.

When the temperature of the 0.5 normal solutions was varied, the color changed from a yellow at low temperatures to a maximum at 80° C. Above this temperature the color again became lighter.

Change of time of striking and of concentration of metal ions seemed to have no appreciable effect on the color of the chromate pigments.

Acknowledgment

The authors wish to express their appreciation to the Oil, Paint, and Varnish Club of Louisville for their financial contribution in this research, and to Andrew Snyder for his valuable suggestions and aid.

Literature Cited

(1) Bergh, *Apoth. Ztg.*, **24**, 291 (1909).
(2) Bülmann, *Ann. chim. phys.*, **9**, 15, 109 (1921); **16**, 321 (1921).
(3) Fresenius and Cohn, "Quantitative Chemical Analysis." Vol. II, pp. 599–600, Wiley, 1915.
(4) Kolthoff, *Pharm. Weekblad*, **57**, 252–65 (1920).
(5) Langnecker, *Biochem. Z.*, **122**, 34–8 (1921).
(6) Sörensen, *Ibid.*, **21**, 131 (1909).
(7) Westberg, *Z. physik. Chem.*, **4**, 150 (1889).

Apparatus and Methods for Precise Fractional-Distillation Analysis[1]

New Method of Gas Analysis

Walter J. Podbielniak

1207–8 Medical Arts Bldg., Tulsa, Okla.

The history of development of the Podbielniak apparatus for precise fractional-distillation analysis is outlined, including a complete survey of low-temperature fractionation methods described in the literature. A comprehensive description is given of the apparatus and analytical procedures in their present state of development, including such topics as accuracy limitations, checking methods, sampling, and interpretation of results. Precision-type fractionating columns are described for the first time; columns of the general design shown may be used to separate highly complex mixtures of saturated and unsaturated gaseous hydrocarbons into their individual components with high accuracy and in short time.

Numerous fractional-distillation curves and check comparisons are given to show the performance of the apparatus on various kinds of gaseous and liquid mixtures. The apparatus and method are widely used in the manufactured-gas, natural-gas, and petroleum industries; they are presented in this article as an accurate analytical tool for the complete analysis of gaseous (or volatile liquid) mixtures of all kinds, which are too complex for the conventional tests.

LITTLE work has been done on the fractional distillation of complex normally gaseous or very volatile mixtures owing, undoubtedly, to the practical difficulties encountered in condensing and fractionally distilling compounds with boiling points far below atmospheric. Pioneer work was done by Ramsay and Travers in their classic study of the gaseous elements found in the atmosphere, as described in 1901 by Travers (*33*). Their procedure for the separation and analysis of argon, nitrogen, oxygen, and other gases consisted in condensing the gas sample at very low temperatures and separating it into fractions by repeated simple distillations from bulb to bulb, the bulbs being held at regulated low temperatures.

In 1915 Burrell, Seibert, and Robertson (*3*) developed an apparatus similar to that used by Ramsay and Travers, with which, for the first time, natural gas was separated into the individual paraffin hydrocarbons present. The analytical procedure was, however, tedious and time-consuming. No fractional-distillation column was used and fractionation was obtained only by repeated simple distillations at very low temperatures and pressures. Slow-combustion analysis was relied on to analyze the resulting binary fractions of hydrocarbons.

In order to shorten the time necessary for an analysis, Shepherd and Porter (*31*), in 1923, developed an apparatus on the same principle as Burrell's but designed to shorten the number of manipulations and time required. The apparatus described is, however, much more complex than that of Burrell's and the procedure, likewise, involved and exacting. The application of the apparatus has, therefore, been restricted mainly to special research work. No fractionating column is used and the fractionation obtained is not sufficient to separate butanes from pentanes or to determine the individual isomers, isobutane and isopentane.

In 1929, Shepherd contributed a later article (*30*) in which he presents his analytical apparatus and method for reference, standardization, and investigations in the determination of gasoline content of natural gas. Analyses of typical natural gases made with his apparatus are compared with the results of the charcoal and oil-absorption methods. No details are given of the comparison tests, nor a comparison made with the California charcoal test (30 pounds at 32° F., or 13.6 kg. at 0° C.); the obsolete oil-absorption test is included; other methods for fractional-distillation analysis for determining gasoline content of natural gas are not considered. The analytical apparatus and methods suggested for determining gasoline content of natural gas appear too complicated and involved for general use in the industry, and apparently the apparatus is not adapted to the accurate determination of pentanes and heavier and of butanes as separate fractions.

Frey and Yant (*7*) used a slightly modified Shepherd and Porter apparatus in 1927 for the analysis of gases from low-temperature carbonization of coal into the individual low-boiling hydrocarbons present. Fractions obtained from a sample using the Shepherd apparatus were further analyzed individually, using standard absorption and other chemical tests to determine hydrogen sulfide, carbon dioxide, nitrogen, oxygen, hydrogen, carbon monoxide, ethylene, ethane, propylene, propane, butylene, butane, and liquid hydrocarbons. They reported further on their investigation (*8*), giving the details of their analytical procedure for the separation of butane-and-heavier fraction. A fractionating column was used for this purpose, described as 50 cm. long, 9 mm. inside diameter, vacuum-jacketed, and filled with 5-mm. brass rings. A hydrogen-vapor cryostat was used for reflux cooling. The redistilled C-4 fraction was brominated, and the bromine addition compounds fractionated at reduced pressures to identify the hydrocarbons originally present.

In a later article (*9*) additional details were given on the combination of the Shepherd and Porter apparatus with an auxiliary fractionating column and Orsat tests to analyze coal gases.

In 1929 Davis (*5*) reported on his investigation for the estimation of unsaturated hydrocarbons in gases including a description of a spiral fractionating column surrounded by a silvered vacuum jacket. The spiral column tube was 3 to 5 meters long and 5 mm. in diameter, coiled into 30 to 50 coils with low pitch. A special thermometer was used for vapor-temperature measurement. The lowest temperature used was −70° C. obtained by mixing solid carbon dioxide with acetone. Distillate fractions were collected as liquid in calibrated glass bulbs immersed in cooling baths. Comparative tests with other columns on standard toluene-benzene mixture showed fairly good separation. Fractional-distillation curves were not shown. In the distillation of

[1] Received September 21, 1930. Presented before the Division of Petroleum Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

the standard benzene-toluene mixture, a sample of 100 cc. and a distillation rate ranging from 30 drops per minute to 1 drop per minute (the lower rate at the transition between benzene and toluene) were used. Heating was accomplished electrically with an immersion-type heater. The apparatus, as described, is not suitable for analysis of gases containing lower boiling hydrocarbons than ethane.

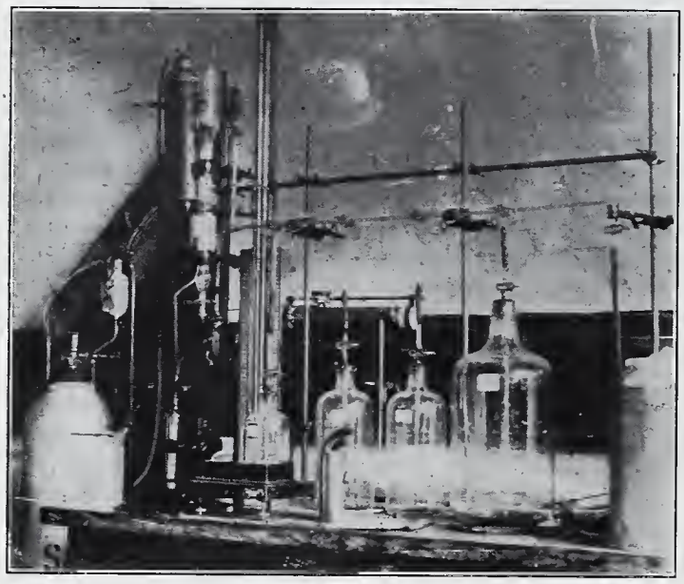


Figure 1—Original Apparatus for Fractional-Distillation Analysis of Natural Gasoline

The author first began work on low-temperature fractional-distillation analysis at the University of Michigan in the summer of 1925, under the guidance of E. H. Leslie (*16*). The first apparatus developed for the fractionation of natural gasoline is shown in Figure 1. As the result of continued research, this apparatus was developed to the point where it was found satisfactory for routine use in the practical operation of natural-gasoline plants (*2*). In 1928, acting upon the initiative, and with the coöperation of the California Natural Gasoline Association, the author prepared three papers pertaining to the standardization and practical applications of the method of analysis (*17, 18, 19*). The general theory of the analytical apparatus and method as developed at that date were also described (*20, 21*) in 1929 as well as its adaptation for accurate determination of gasoline content of dry natural gas (*22*).

The use of this method of analysis for fundamental research on complex solutions at the University of Michigan has been reported (*23*). This work was later continued by Rogers and Brown (*28*), resulting in quantitative measurement of deviations of saturated hydrocarbons from Raoult's law for definite mixtures studied. Hill (*10*) compared the fractional-distillation test with the California charcoal test in the determination of gasoline content of a large number of wet and dry natural-gas samples. Robinson (*26*) wrote a paper on the fundamental theory and computations of an oil absorber based on fractional-distillation analyses, illustrations being given of experimental applications of the theory. Kallam (*11*) discussed the precautions to be taken in sampling, in entering samples into the apparatus, and the need for standardization of sampling and analytical procedures so that results obtained by different laboratories would be strictly comparative. The author (*24*) has presented a detailed discussion of the principles, possibilities of errors, efficient operation, accuracy, and sensitivity of the fractional-distillation analysis apparatus, also its application to the complete analysis of refinery cracked gases and gasolines (*25*). Robinson discusses the use of fractional-distillation analyses in the control of natural-gasoline fractionating towers (*27*).

Recently Schaufelberger (*29*) has given the results of an investigation on the fractionation analysis of hydrocarbon mixtures. From 1923 to 1926 work was done on fractional distillation from activated charcoal, while the investigation of fractional-distillation analysis of gasolines and gas condensates was apparently begun some time in 1926. The apparatus described by Schaufelberger is very similar in principle to the author's. Schaufelberger's fractionating column, while in the main similar to the Regular column to be described in this article, is made up of two parts: the fractionating vacuum-jacketed column proper, and a separate reflux chamber, the two joined by a cork. A gasoline bath is used in the reflux chamber, agitated with a turbine-type stirrer. The column vacuum jacket is silvered completely except for one window at the drip indicator, the latter being placed high in the fractionating column. This style of silvering provides somewhat better thermal insulation over a strip-silvered column, but also decreases visibility and ease of control. A potentiometer is used with a thermocouple for vapor-temperature measurement in preference to a millivoltmeter. As regards the size of sample needed, this seems to be comparable to that required with the author's apparatus, except that very much larger samples of dry natural gas are needed (up to as much as 75 liquid cc.). No information is given as to the time of analysis required and as to the accuracy of the analytical results obtained.

Note—This drip indicator is similar to that described by H. S. Davis (*5*), except that Davis' indicator is located at the bottom of the column which is preferable, inasmuch as a drip indicator high up in the column introduces an objectionable and unnecessary hold-up of liquid very near the point where fractionated vapor is taken off from the column.

Additional references (*1, 4, 6, 12, 13, 15, 32, 34*) complete the bibliography for the apparatus and methods for low-temperature fractional-distillation analysis.

Description of Apparatus

At present the apparatus developed by the author is widely used in the natural-gas, natural-gasoline, and petroleum-refining industries for research and routine analysis of gaseous and liquid hydrocarbon mixtures. Figure 2 shows a double-unit apparatus as used in industrial laboratories, one unit of the apparatus being specially adapted for gas analysis and the other for liquid analysis.

Figure 3 is a diagram of the apparatus for fractional-distillation analysis. Briefly, it consists of a vacuum-jacketed fractionating column, designed for highest possible fractionating efficiency at reflux temperatures below atmospheric and of accessory apparatus for suitable introduction of gas or liquid samples into the column, and for temperature and distillate measurement.

Fractionating Columns—The column is constructed of Pyrex and entirely vacuum-jacketed, as shown in the diagram. The column tube proper is about 3.8 mm. in diameter and about 77 cm. long. The vacuum jacket is silvered opaque, leaving only two narrow clear strips along the length of the column on opposite sides for observation. The distilling bulb is almost entirely insulated thermally by the vacuum jacket, and heat is supplied to it by means of an external resistance wire heater, as shown. A drip indicator is provided at the bottom of the column tube, from which droplets of refluxed liquid fall and may be counted per unit time. The little holes in the sides of the drip indicator are necessary to avoid flooding of column and trapping of vapor in the upper part of the distilling bulb. Davis (*5*) describes a similar drip indicator which, however, would not be satisfactory for use with a 3.8-mm. column, as it has no vent holes for vapor. A hairpin precooling tube is pro-

vided at the bottom of the column, and may be immersed in a cooling bath when a gaseous or volatile-liquid sample is being entered into the column.

The detail of the column packing is shown in Figure 3. The unusual feature of this type of packing is that the refluxed liquid is distributed into very thin capillary films supported only at their boundaries by the turns of the wire coil and by the glass walls, instead of simply wetting the very small surface of the packing. This results in maximum contacting between liquid and vapor with least hold-up of liquid on the packing, conforming to the requirements of the most efficient column packing for analytical distillation. The wire coil is also filed or ground on the outside to avoid further accumulation of liquid in the interstices between the turns of the wire and the glass walls of the column. It has been found by extensive experimentation that the diameters of the column and packing given are most conducive to best fractionating efficiency of the column. It is obviously desirable to have the packing fit the column tube as snugly as possible.

Other modifications of this type of coil packing may be used, but the single-wire-coil type has been found most practical for general use.

It will be noted that there is no opportunity for superheating of vapor arising from the boiling sample in the still. This is important in fractionating low-boiling compounds, as any such superheat would decrease the usefulness of the lower part of the column.

In the column shown in the diagram, reflux cooling is accomplished by blowing liquid air or other refrigerant into the cooling vessel which is immersed in a suitable gasoline or other liquid bath. The vapor temperature was formerly measured with a triple-junction copper-constantan thermocouple connected to a sensitive millivoltmeter. Recently it was decided to use a single-junction thermocouple, as it could be more easily centered in the vapor-delivery tube of the column, and as it should be somewhat more accurate owing to its smaller size, fewer wires, and less chance of short circuit. An extra-sensitive millivoltmeter was developed by a manufacturer to give the same scale deflection per unit temperature difference between hot and cold junction, using the single-junction thermocouple, as was obtained previously using a triple-junction thermocouple and a less sensitive millivoltmeter. A potentiometer may, of course, be used instead of a millivoltmeter.

The most satisfactory way to calibrate a thermocouple was found to be by plotting observed millivoltage obtained with the thermocouple against the known boiling points of the lower boiling hydrocarbons separated in analytical distillations. A small thermocouple is by far the most satisfactory device for measuring temperature in this work. A thermometer would not be accurate enough even if one could be made small enough and of sufficient temperature range. A resistance thermometer is too cumbersome and has too high a capacity for heat, as well as other disadvantages.

Figure 4 shows two forms of another type of fractionating column developed by the author for use with the apparatus. These are called Precision-type columns because of their increased fractionating efficiency and greater sensitivity over the Regular-type column.[2] Column *L* is so constructed that the column tube is continuous and in one piece with the vapor-delivery tube, but sealed to the vacuum jacket at the top of the distilling bulb. In column *R*, the column tube, together with distilling bulb and connections, is entirely separate from the vacuum jacket, which latter becomes merely a sleeve for thermal insulation only. The air space between the column tube and the inner tube of the vacuum jacket introduces no objectionable effects and, in fact, slightly increases the thermal insulation around the column. Instead of using a gasoline bath in the reflux chamber, a special liquid-air cooling vessel is packed snugly into the reflux chamber using dry asbestos fiber. Heat transfer is accomplished through the medium of fine copper powder or other heat-conducting material, filling the annular space between the inner tube of the cooling vessel and the column tube proper. It has been found, however, that sufficient heat transfer is obtained without any filling of metallic powder. The heat capacity of the reflux cooling vessel may be increased by adding glass beads through one of the outlet tubes, although this is not usually necessary.

For use in the analysis of gases containing methane or lower boiling hydrocarbons, the cooling vessel is provided with two additional tubes, *B*, leading below the cooling vessel proper. The refrigerant may thus be brought into direct contact with the glass wall of the column tube, securing lower reflux temperature than would be possible with tubes *A* or through the medium of a gasoline bath. Tubes *B* are used only at the beginning of distillation of very volatile gases, as tubes *A* are preferable for close reflux temperature control.

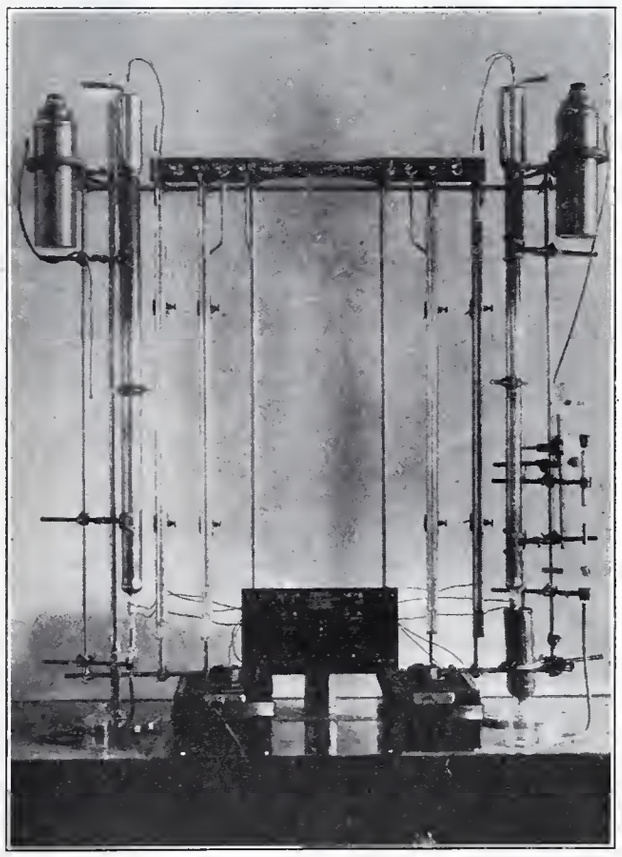


Figure 2—Improved Double-Unit Apparatus

The Precision-type columns are otherwise similar to the Regular-type columns previously described, and are operated similarly, with slight variations in procedure to take care of different column characteristics. The Precision-type columns, because of less hold-up of vapor and liquid, and because of the somewhat greater length of packing possible for the same over-all length, show much more efficient fractionation, especially in the case of small samples. It will be noted that Precision *L* and Precision *R* columns differ only in the bottom construction. Precision *L* column is more compact and the distilling bulb has built-in thermal insulation. Precision *B* column requires the use of cork or other supports for the column tube and an insulating thermos tube; on the other hand, its two-part construc-

[2] The apparatus and fractionating columns described in this article are covered by pending applications for patents.

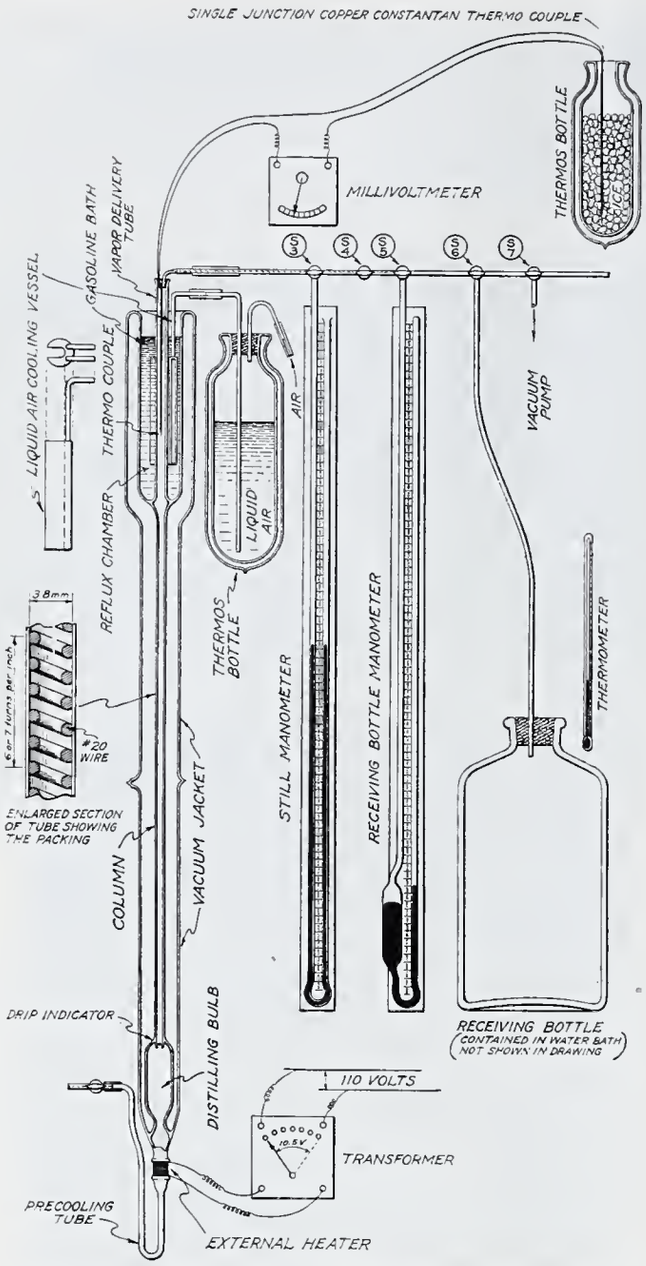


Figure 3—General Diagram of Apparatus with Regular-Type Fractionating Columns

tion makes possible the use of different column assemblies interchangeably in the same vacuum sleeve and reflux chamber.

By filling the distilling bulb of either Precision column with mercury, the total volumetric capacity of the column is reduced to less than 6 cc., which greatly increases the sensitivity of the column to very small samples, as in the case of determining the pentanes-and-heavier content in very dry natural-gas samples. It may be pointed out here that this method of increasing the sensitivity of the columns when required, by decreasing the hold-up of liquid and vapor, is much more practical and accurate than the provision of a very small auxiliary column as used in a few laboratories.

Owing to the more efficient reflux arrangement, the consumption of liquid air using a Precision-type column is materially less than with the Regular column [usually only about 1 liter to 1.5 liters of liquid air per 5-gallon (18.9-liter) natural-gas sample, including the liquid air used for precooling the sample]. The column tube in the Precision column is flexible and adequately protected by the cooling vessel so that breakage from mechanical shock will not result even from careless handling. The distilling bulb of either type column is made as small as compatible with the purpose for which the column is to be used, in order to decrease unnecessary vapor hold-up. Columns of both types may be adapted to the use of liquid carbon dioxide as refrigerant which may be expanded directly into either the Regular or Precision type of cooling vessel.

It is important to reduce to a minimum the dead vapor space from the thermocouple junction to stopcock 4 (Figure 3), as this space introduces a lag between the measurement of vapor temperature at the thermocouple junction, and between the measurement of amount of distillate beyond stopcock 4. This is accomplished by using a fine flexible metal tube (about 1.5 mm. i. d.) as a connection from the top of the column to the stopcock manifold, and by using semi-capillary stopcock tubes in that part of the manifold to the left of stopcock 4.

Collection and Measurement of Distillate—The distillate from the column passes in vapor form through the fine metal tube to the stopcock manifold and into any one of two or more glass bottles previously evacuated to a pressure considerably below distillation pressure. Since the amount of distillate must be computed accurately from the known capacity and increase in pressure in the receiving bottle, it is essential that this part of the system be designed for an accuracy of measurement not less than about 0.03 per cent of the volume of distillate measured (for industrial testing purposes). While a small bottle, for instance, 1-gallon (3.78-liter) size, is more accurate in that a small amount of distillate passed into it results in a large rise in pressure, it soon fills with vapor and must be reëvacuated perhaps several times during an ordinary analysis. A 3-gallon (11.35-liter) or 2-gallon (7.57-liter) bottle was therefore adopted for general use, together with a bulbed barometric-type manometer as shown in Figure 3, to measure the pressure of the vapor distillate. This type of manometer restricts practically all the movement of the mercury to the closed arm, and is almost twice as sensitive to changes in pressure as the ordinary U-type previously used. Using a 2-gallon (7.57-liter) bottle with this manometer, each millimeter on the closed arm of the manometer corresponds to approximately 10 cc. of vapor at room temperature and 760 mm. pressure (the exact ratio depends on the bottle calibration); or each estimated tenth of a millimeter corresponds to 1 cc. of vapor. This is sufficiently accurate when the usual sample of 4000 cc. or more is taken for analysis.

The use of 5-gallon (18.9-liter) and larger bottles is advised against by Rogers and Brown (*28*), who find that large bottles show appreciable contraction when evacuated.

Connecting copper tubing and stopcocks beyond stopcock 4 may be considered part of the vapor-receiving bottle and should be included in the calibration. A small-bore barometric manometer should be used to minimize the error caused by variation of space in its open arm.

Each degree Centigrade change in the temperature of the vapor in the receiving bottle will change its pressure approximately 0.33 per cent. All the vapor-receiving bottles are therefore placed either in a special constant-temperature water bath, or simply in a large tank of water to keep the vapor temperature practically constant.

The volumetric capacity of the connections is kept fairly small, so that temperature changes around the connections will have no appreciable effect on the pressure of the total vapor-receiving system.

It will be noted in the diagram (Figure 3) that the apparatus is made up of separate parts connected by copper or rubber tubing. Any part may be taken out for repair or replacement and another part put in its place without requiring the services of a glassblower or trained laboratory technician. Fused-glass joints are not required in the apparatus since its

operation does not involve greater vacuum than about 2 or 3 mm. of mercury absolute. Leaks will not occur often if all connections are made up with the best grade of medium heavy-walled rubber tubing with the aid of clear Duco or a little shellac.

Outline of Analytical Procedures

The operation of the apparatus may be varied to permit analytical distillation of components of varying volatility from methane or even lower boiling hydrocarbons, liquefiable at liquid air temperature and atmospheric pressure, to hexanes and heptanes. These latter are distilled at pressures as low as 20 mm. absolute, so that the reflux temperature always remains below atmospheric. In general, it is most practical and convenient to conduct distillation at atmospheric pressure whenever possible, in order to avoid correction of boiling points and to minimize the possibility of errors due to leaks in the apparatus. Distillation pressures have been standardized as shown in Table I.

Table I—Standard Distillation Pressures

Hydrocarbon	Column Pressure *Mm.*
Methane, ethane, propane, butanes, and compounds of boiling points lower than atmospheric temperature	Atmospheric
Pentanes, amylenes	300 abs.
Hexanes, hexenes	100 abs.
Heptanes	20 abs.
Octanes and heavier	(Not usually practicable to distil, as very low pressures and frequent reëvacuations of vapor-receiving bottles are necessary)

Note—Reflux temperature should never be allowed to equal or exceed or even to come close to room temperature.

However, it is entirely feasible to conduct distillations at lower pressures than those recommended or even to conduct isothermal distillations if required for special purposes.

As already mentioned, the distillate is usually collected in vapor form in evacuated glass bottles. The amount of distillate is computed from the calibrated volume of the glass bottle and from the temperature and pressure of the contained vapor, using known physical constants and ideal gas laws. In order to avoid errors introduced by the deviations of heavier hydrocarbons from ideal gas laws (*28*), the hydrocarbons are collected below standard maximum partial pressures as shown in Table II.

Table II—Maximum Partial Pressures in Vapor-Receiving Bottle

Hydrocarbon	Max. Partial Pressure *Mm.*
Methane	Atmospheric
Ethane	Atmospheric
Propane	Atmospheric
Butanes	400 abs.
Pentanes	80 abs.
Hexanes	20 abs.
Heptanes	5 abs.

Once a sample is entered into the column, the analytical procedure is essentially the same, whether the sample is natural gas, coal gas, liquefied petroleum gas, natural gasoline, or ordinary motor fuel. The pressure in the column is brought to atmospheric by applying heat to the distilling-bulb heating element (regulating with the transformer shown), or by cooling the reflux with liquid air, depending on whether the column pressure is below or above atmospheric. The vapor formed passes up the column and is condensed at the reflux. In order to maintain this flow of reflux liquid down the column it is necessary to extract heat from the reflux by periodically blowing more liquid air into the reflux cooling vessel. The supply of current to the column-heating element and the cooling of the reflux should be so balanced that (1) the column pressure is practically atmospheric, and (2) the entire wire packing of the column is wet with the minimum amount of reflux to form capillary liquid films.

If the vapor temperature shows a tendency to rise above room temperature before the pressure in the column becomes atmospheric, it will be necessary to begin the distillation at a lower pressure in accordance with Table I, as otherwise the overhead vapor from the column will condense in the capillary connections.

When the proper conditions have been established in the column, distillation may be commenced by cracking stopcock 4 to allow the fractionated overhead vapor to pass slowly through the stopcock train into the receiving bottle which had been evacuated previously to a fairly low pressure. The barometric manometer connected to the receiving bottle indicates the rise in pressure in this bottle as it fills with vapor. This rate of distillation is controlled by changing the setting of stopcock 4 so as to secure the best possible fractionation compatible with a maximum permissible total time for the distillation. In practice this is equivalent to

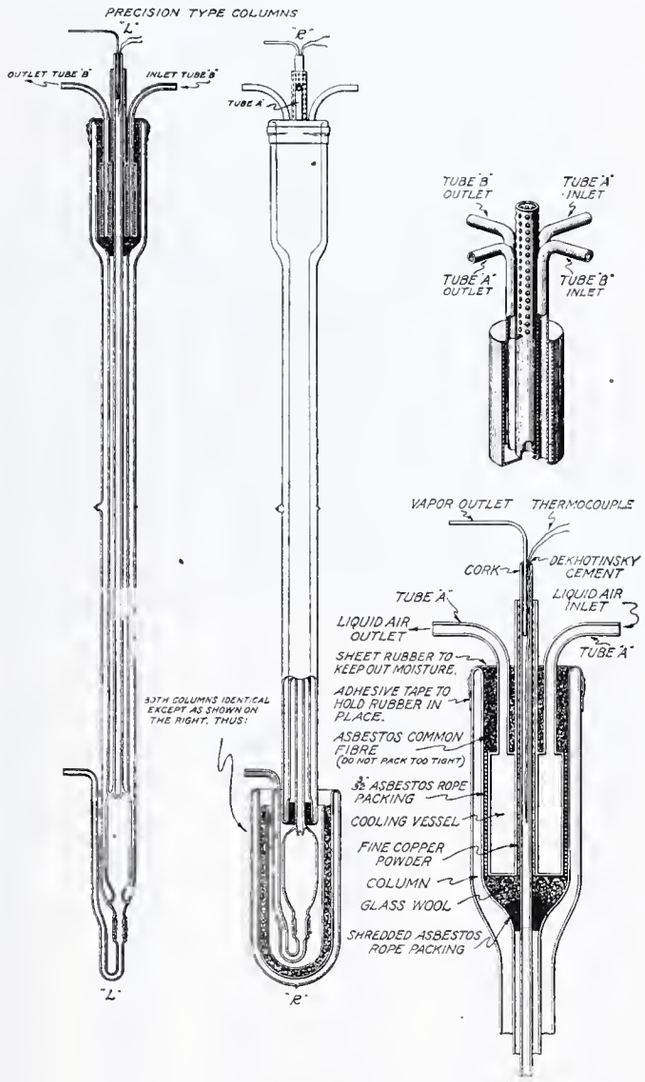


Figure 4—Precision-Type Fractionating Columns

slowing the distillation rate to a very low value whenever the vapor temperature tends to rise at constant pressure, and increasing the distillation rate when the temperature tends to stay constant. In this way, one hydrocarbon after another is distilled with very sharp temperature rises (Figures 5 to 11) until the entire sample is distilled or until an undistillable residue remains. Frequent simultaneous readings, (1) of the thermocouple e. m. f.'s indicated by the millivoltmeter, (2) of column pressure on the open-arm manometer, and (3) of the pressure on the receiving-bottle manometer, are taken to enable the operator to construct subsequently a plot of vapor temperature (corrected to a standard pressure) against the amount of vapor distilled.

Securing Fractions for Supplementary Tests—In the case of highly cracked gases, it may be advisable to supplement the fractional-distillation analysis with further Orsat or other tests on particular fractions. For instance, even the Precision-type column will not separate the individual hydrocarbons in the complex C-4 fraction of highly cracked gases or gasolines. This fraction will normally contain isobutane, *n*-butane, and several isomeric butenes, all boiling within a range of about 15° C. In such cases, the desired fraction or fractions may be taken directly off the stopcock manifold during distillation, between, of course, suitable temperature cut points, and analyzed separately by absorption in suitable reagents, by slow combustion, and by other tests described by the writer (*25*) and by Frey and Yant (*7*, *8*, *9*).

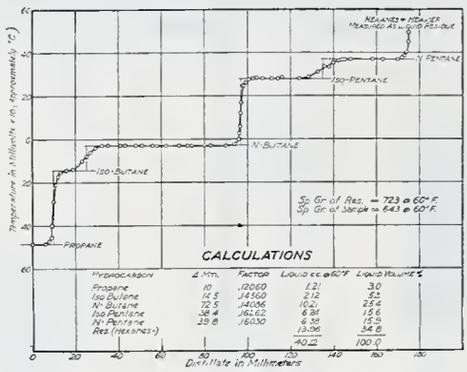


Figure 5—Fractional-Distillation Curve of Natural Gasoline

Calculations for Liquid Analysis

As an illustration of the method used in calculating the results of a gasoline analysis, the data in Table III and the fractional-distillation curve, Figure 5, for a sample of unstabilized natural gasoline are offered.

The data in Table III give the actual readings taken during analysis and the figures calculated from these readings.

Table III—Readings for Fractional-Distillation Analysis of Natural-Gasoline Sample

Vapor Temp.	Column Pressure	Bottle Pressure	Bath Temp.	Cor. Temp.	Calcd. Pressure
Millivolts	*Mm.*	*Mm.*	*° C.*	*° C.*	*Mm.*
−4.9	Atm.	0	26.4	−49.0	0
−4.9	Atm.	6.0	..	−49.0	6.0
−4.8	Atm.	7.0	..	−48.0	7.0
−4.6	Atm.	8.5	..	−46.0	8.5
−4.2	Atm.	9.0	..	−42.0	9.0
−2.9	Atm.	10.0	..	−29.0	10.0
−2.1	Atm.	11.0	..	−21.0	11.0
−1.73	Atm.	12.0	..	−17.3	12.0
−1.52	Atm.	13.0	..	−15.2	13.0
−1.43	Atm.	16.0	..	−14.3	16.0
−1.40	Atm.	18.2	..	−14.0	18.2
−1.0	Atm.	23.0	..	−10.0	23.0
−0.8	Atm.	25.0	..	− 8.0	25.0
−0.6	Atm.	27.0	..	− 6.0	27.0
−0.4	Atm.	29.0	..	− 4.0	29.0
−0.3	Atm.	32.0	..	− 3.0	32.0
−0.28	Atm.	40.0	..	− 2.8	40.0
−0.28	Atm.	80.0	..	− 2.8	80.0
−0.25	Atm.	90.0	..	− 2.5	90.0
−0.23	Atm.	94.0	..	− 2.3	94.0
−0	Atm.	0.0	..	0.0	94.0
....	615–277	2.0	..	0.0	96.0
−1.35	615–277	2.2	26.5	+ 2.0	96.2
−1.0	615–277	2.3	..	+ 6.0	96.3
−0.5	615–277	3.0	..	+12.0	97.0
0	615–277	3.2	..	+17.0	97.2
+0.8	615–277	4.0	..	+24.5	98.0
+1.05	615–277	8.0	..	+28.0	102.0
+1.05	615–277	30.0	..	+28.0	124.0
+1.1	615–277	34.0	..	+28.5	128.0
+1.45	615–277	39.0	..	+31.0	133.0
+1.75	615–277	44.0	26.7	+34.0	138.0
+0.95	675–216	46.0	27	+35.5	140.0
+1.02	675–216	48.0	..	+36.5	142.0
+1.15	675–216	54.0	..	+37.0	148.0
+1.15	675–216	76.0	..	+37.0	170.0
+1.20	675–216	78.0	..	+37.5	172.0
+1.25	675–216	79.0	..	+38.0	173.0
+1.35	680–209	80.0	27	+40.0	174.0
+2.25	675–216	81.0	..	+50.0	175.0

The vapor temperatures at the top of the column are read by the analyst on the millivoltmeter, which is graduated to tenths of a millivolt.

The column-pressure readings on both arms of the open-arm manometer connected to the fractionating column are recorded. When the mercury stands at the same level in both arms, the pressure in the column is atmospheric.

The pressures on the closed arm of the closed-arm manometer connected to the vapor-receiving bottle used in the analysis are recorded as bottle pressure. These readings must be taken with care and estimated to tenths of a millimeter. In both Table III and Table IV two series of bottle-pressure readings are shown. Each series begins with an initial low pressure in an evacuated vapor-receiving bottle, and ends with the maximum permissible pressure in the bottle. After each final reading the bottle is reëvacuated and another series of readings taken. This is done as often as required.

Several times during an analysis, readings (correct to 0.1° C.) are taken of the temperature of the water bath in which the vapor-receiving bottles are immersed. These readings should be taken preferably at the break points on the fractional-distillation curve, as evidenced by sudden temperature rise. Failure to record these readings may lead to considerable error in analysis, especially when the laboratory temperature fluctuates considerably.

The corrected temperatures are obtained by multiplying the vapor-temperature readings by 10 (the calibration curve of the thermocouple should be used for precise work), and converting to temperatures at atmospheric pressure by means of a suitable chart (*17*).

The calculated pressures are obtained from the bottle-pressure readings by the following procedure: The initial reading of the first series in the bottle-pressure column (which is not necessarily zero, as shown in Table III, but will depend on the setting of the meter stick) is subtracted from itself and then successively from every other reading of the series to yield the corresponding calculated pressures. To convert the second series of bottle-pressure readings, the final calculated pressure of the first series is subtracted from the initial reading of the second series (0.0 − 94.0 = −94.0), and from every other reading of the series in succession. The third and following series are converted similarly. The effect of this procedure is to arrange all the millimeter intervals in the bottle-pressure columns of the tables into one continuous series beginning with zero to be proportional at any point to the total volume (in vapor form) of the sample distilled.

The calculated figures are now plotted on suitable graph paper to yield a fractional-distillation curve, as shown by Figure 5.

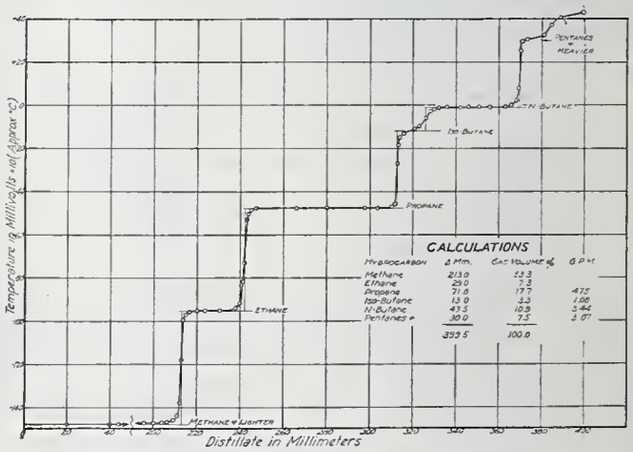


Figure 6—Fractional-Distillation Curve of Natural Gas

If the fractionation obtained with the apparatus were perfect, this curve would consist of perfectly horizontal plateaus and of perfectly vertical and rectangular rises in temperature. The curves actually obtained approximate this ideal quite closely, except in the case of compounds with boiling points not far apart, which are difficult to separate by fractional distillation. In order to determine the proper cut points on the temperature rises in the curve, the so-called "equal-area" method, described in a previous article (*21*), is used. The mid-point method of locating

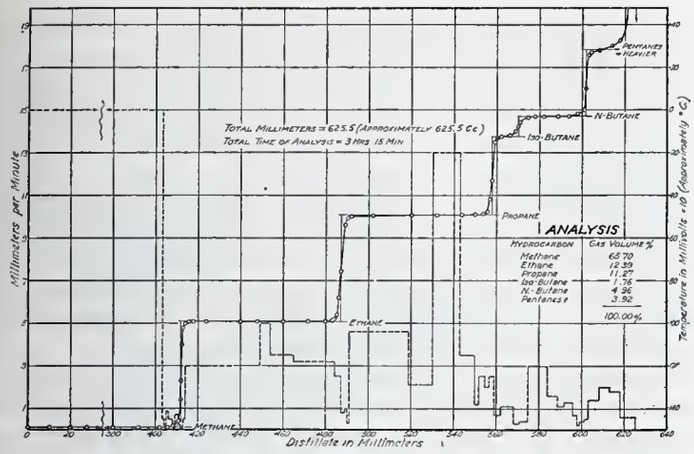


Figure 7—Analysis of Typical Wet Natural Gas Showing Time-Rate *vs.* mm. Curve

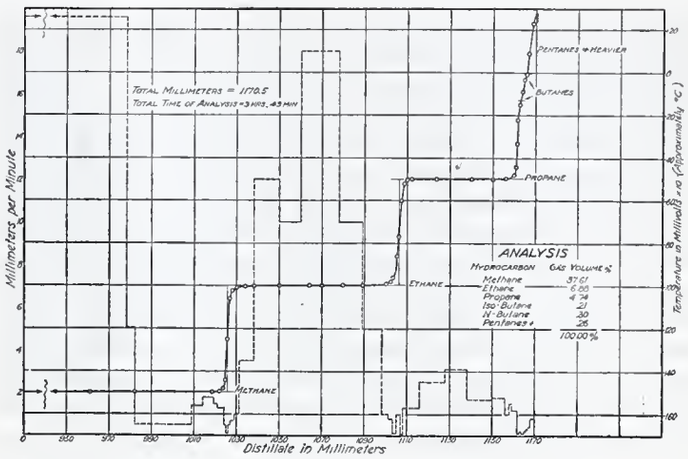


Figure 8—Analysis of Typical Residue Natural Gas Showing Time-Rate *vs.* mm. Curve

cut points has no theoretical justification and should not be used except for very sharp temperature rises.

Each plateau on the curve corresponds to a pure hydrocarbon and is identified by its boiling point. The amounts of the hydrocarbons are proportional to the lengths of these plateaus. The length of each plateau is taken equal to the distance between its cut points (Δ mm.) and multiplied by the proper factor to convert it to cubic centimeters of the liquid hydrocarbon at 60° F. (15.56° C.). The residue or non-distilled portion of the sample has already been measured in liquid cubic centimeters and its (liquid) volume is merely corrected for temperature to 60° F. (15.56° C.). To obtain the liquid-volume percentages of the hydrocarbons in this sample, simply divide the volume in liquid cubic centimeters of each hydrocarbon by the sum of these volumes, and multi-

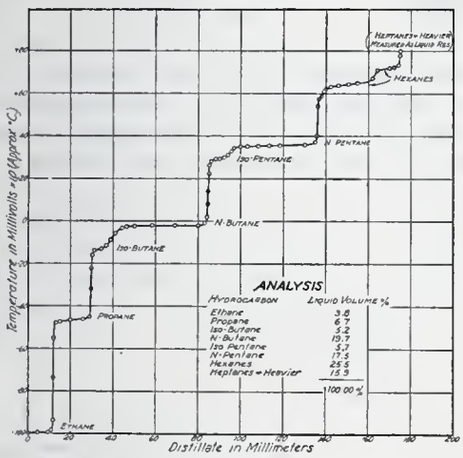


Figure 9—Typical Analysis of Natural Gasoline Using Precision-Type Column

ply by 100. To obtain mol per cent, convert the residue to millimeters rise in mercury on the closed-arm manometer, using the proper factor, and divide each Δ mm. by the sum of these Δ mm.'s, including the calculated one for the residue. This is done on the assumption that the temperature of the water bath has been constant for the entire analysis. Gas-volume per cent and mol per cent can be considered identical for most practical calculations.

The factors for the conversion of millimeters rise of mercury on the closed arm of the closed-arm manometer to cubic centimeters of liquid hydrocarbon are calculated by the following formula, based on ideal gas laws and known physical constants:

$$\frac{2K}{760} \times \frac{273\,H}{22410\,(273 + VT)} \times \frac{MW}{\text{sp. gr. (60° F.)}}$$

where K = correction factor for inequality of bore of two arms of the closed-arm manometer

H = volume of vapor-receiving bottles and connections

VT = temperature in ° C. of water bath containing vapor-receiving bottle

MW = molecular weight of hydrocarbon identified by its boiling point

Sp. gr. (60° F.) = specific gravity of liquid hydrocarbon at 60° F. (15.56° C.) standard temperature used in petroleum industry

In calculating these factors and in other calculations, a Table of Physical Constants (*17*) and the National Standard Petroleum Oil Tables (*14*) were used for correcting specific gravities and liquid volumes for temperature.

Calculations for Gas Analysis—The calculations for gas analysis (Table IV and Figure 6) are exactly the same as for liquid analysis except that there is no liquid residue, and it is sufficient simply to divide each Δ mm. by the sum of the Δ mm.'s for the whole gas sample, and to multiply by 100 to obtain the gas-volume per cent.

Table IV—Readings for Fractional Distillation Analysis of Natural-Gas Sample

Vapor Temp.	Column Pressure	Bottle Pressure	Bath Temp.	Cor. Temp.	Calcd. Pressure
Millivolts	*Mm.*	*Mm.*	*° C.*	*° C.*	*Mm.*
−15.0	Atm.	0	23.5	−150.0	0.
−14.7	Atm.	200.0	..	−147.0	200
−14.7	Atm.	204.0	..	−147.0	204
−14.7	Atm.	206.0	..	−147.0	206
−14.6	Atm.	209.2	..	−146.0	209.2
−14.4	Atm.	211.0	..	−144.0	211.0
−13.8	Atm.	212.0	..	−138.0	212.0
−11.8	Atm.	213 0	23.5	−118.0	213.0
− 9.95	Atm.	213.5	..	− 99.5	213.5
− 9.7	Atm.	215.0	..	− 97.0	215.0
− 9.6	Atm.	217.0	..	− 96.0	217.0
− 9.6	Atm.	231.0	..	− 96.0	231.0
− 9.4	Atm.	238.0	..	− 94.0	238.0
− 9.2	Atm.	240.0	..	− 92.0	240.0
− 8.2	Atm.	241.2	23.5	− 82.0	241.2
− 7.4	Atm.	242.0	..	− 74.0	242.0
− 5.3	Atm.	243.0	..	− 53.0	243.0
− 5.0	Atm.	243.5	..	− 50.0	243.5
− 4.9	Atm.	245.0	..	− 49.0	245.0
− 4.8	Atm.	247.0	..	− 48.0	247.0
− 4.8	Atm.	266.0	..	− 48.0	266.0
− 4.8	Atm.	280.0	..	− 48.0	280.0
− 4.8	Atm.	304.0	..	− 48.0	304.0
− 4.75	Atm.	310.0	..	− 47.5	310.0
− 4.6	Atm.	312.0	..	− 46.0	312.0
− 2.7	Atm.	313.0	23.5	− 27.0	313.0
− 1.9	Atm.	313.5	..	− 19.0	313.5
− 1.5	Atm.	314.0	..	− 15.0	314.0
− 1.3	Atm.	316.0	..	− 13.0	316.0
− 1.1	Atm.	321.0	23.5	− 11.0	321.0
− 1.0	Atm.	322.5	..	− 10.0	322.5
− 0.30	Atm.	328.0	..	− 3.0	328.0
− 0.20	Atm.	330.0	..	− 2.0	330.0
		0.0	23.5		330.0
− 1.70	600–263	4.0	..	− 1.2	334.0
− 1.65	600–263	26.0	..	− 1.0	356.0
− 1.55	600–263	36.0	..	0	366.0
− 1.35	600–263	38.0	24	+ 2.0	368.0
− 0.85	600–263	39.0	..	+ 8.0	369.0
+ 0.80	600–263	40.0	..	+ 25.0	370.0
+ 1.35	600–263	41.0	..	+ 30.0	371.0
+ 1.40	600–263	43.0	..	+ 30.5	373.0
− 1.2	735–108	51.0	..	+ 32.0	381.0
− 0.75	735–108	54.5	..	+ 37.0	384.5
− 1.7	759–80	59.0	..	+ 41.0	389.0
− 1.6	759–80	69.5	24	+ 43.0	399.5

By the use of proper physical constants and conversion factors (*19*), it is possible readily to convert gaseous-volume

per cents to liquid-volume per cents and vice versa, and also to convert gas-volume per cents to GPM's (gallons per 1000 cubic feet of the gas at standard conditions). To calculate the GPM of a gas from gas analysis (as in the determination of gasoline content of a natural-gas sample), it is only necessary to divide the per cent of pentanes and heavier as obtained from gas analysis, by the number of cubic feet of hexane vapor at 14.7 pounds per square inch pressure (approx. 1 kg. per sq. cm.), and 60° F., equivalent to 1 gallon of liquid hexane at 60° F. (3.78 liters at 15.56° C.) (*17*), and to multiply the result by 10. The resulting figure represents the GPM of pentanes and heavier recoverable from the gas. It may in turn be converted to GPM of gasoline of a specified composition such as 35 per cent butanes, by dividing the GPM of pentanes and heavier by 0.65.

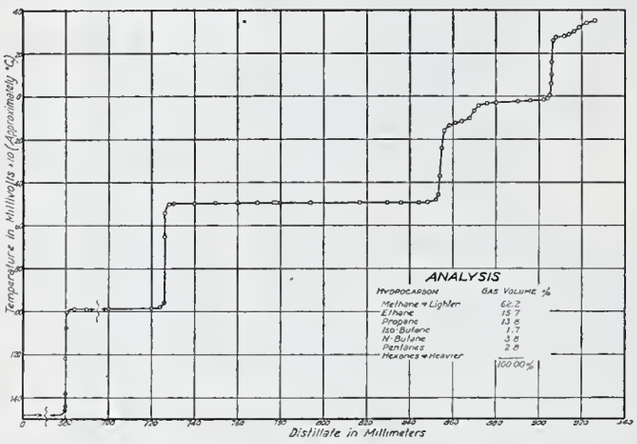


Figure 10—Typical Analysis of Natural Gas Using Precision-Type Column

The use of a hexane factor or factors for pentanes and heavier should be used with judgment. In the case of residue gases from gasoline plants, it may be more accurate to use a pentane factor for the heavier-than-butane residue. In any case, the error introduced is usually small and may be minimized by continuing the distillation so as to determine pentanes separately and hexanes and heavier, which latter would be considered equivalent to heptane. The error would thus become negligible.

In addition to the calculations strictly necessary to obtain analytical results, it is advisable to take frequent time readings during the analysis and to plot the distillation time rate (in millimeters rise of mercury per minute on the closed-arm manometer) against the amount of distillate (in millimeters rise of mercury on the closed-arm manometer), as shown in Figures 7 and 8. Contrary to usual distillation practice, the rate of distillation is not kept constant, but is varied according to the difficulty of fractionation so as to yield the best possible fractionation in a given time per analysis. It will be seen that the rate of distillation is greatly increased when on a plateau of the curve—that is, when a pure component is easily distilled without change in boiling point—and progressively decreased to almost zero at transition points when the last traces of lower boiling component are being separated from the next higher boiling component. The aim of the operator of this apparatus should be to save time by increasing the rate of distillation, whenever this is possible, without raising the vapor temperature, and by progressively decreasing this rate as fractionation becomes more difficult, to obtain sharply defined breaks between components. This is the correct theoretical procedure and is completely substantiated by practice.

Incidentally, such curves furnish a valuable guide to one learning the operation of the apparatus, as he need only follow the standardized curves of time-rate versus pressure for various gas and gasoline samples in order to master the proper regulation of the rate of distillation.

It will be noted that a very high rate may be used for the entering of a gas sample into the column, as the separation of methane from ethane at low temperatures is unusually easy.

Figures 9, 10, and 11 show the superior fractionating efficiency that may be obtained with the Precision column on various samples. Close-boiling hydrocarbons such as ethylene and ethane, propylene and propane, isobutane and *n*-butane, and isopentane and *n*-pentane are fairly well separated in a single analytical distillation.

Figure 12 shows an interesting curve which was obtained by a single distillation of a synthetic mixture of pure organic compounds as indicated, using a modified Precision-type column. The separation obtained is equivalent to that obtained by previous experimenters after a large number of redistillations upon a large sample of gasoline, using ordinary laboratory fractionating columns.

Sampling into the Apparatus

Size of Sample—About 50 cc. is the usual volume of gasoline or other liquid sample used with the apparatus. Gas samples of 6000 cc. should perhaps be considered the minimum for good general fractionation analysis. In the case of determination of gasoline content in natural gas, the empirical rule given in Table V may be found useful.

Table V—Size of Gas Sample

Minimum Size of Sample	Estimated Pentanes and Heavier	
Cc.	*%*	*GPM*
4,000	2.44	1.0
8,000	1.22	0.5
20,000	0.49	0.2
40,000	0.24	0.1
80,000	0.12	0.05

The above recommendations are based on the assumption that a large gas sample is easily obtainable, and that the maximum accuracy of the determination of pentanes and heavier is required without need for any change in analytical procedure or special care beyond that ordinarily required in routine analysis. However, it is possible to get sufficient accuracy and sensitivity with a very much smaller sample when necessary, especially with precision columns. The above values are very conservative and intended merely as a safe general guide.

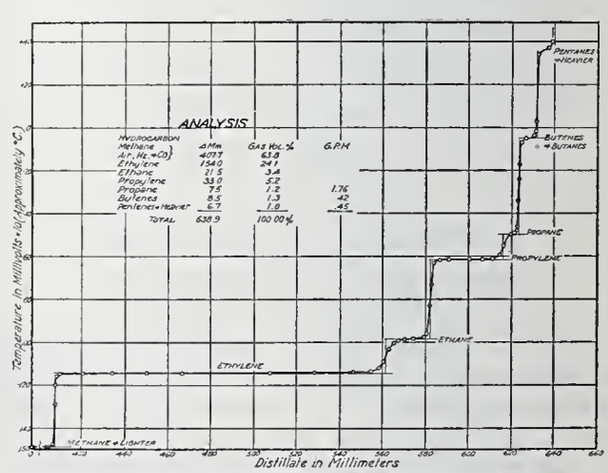


Figure 11—Typical Analysis of Refinery Cracked Gas Using Precision-Type Column

Gas or liquid samples are entered into the previously evacuated column of the apparatus, stopcock 4 being, of course, closed at this time, except when methane and lighter compounds are intentionally vented simultaneously during sampling in order to save time on distillation, as described

in a previous article (*22*). The reflux is cooled sufficiently to condense the lowest boiling component in the sample if possible. The transfer of volatile liquid mixtures to the column necessitates special attention to avoid change of composition in the sampling or transfer of such liquids as, for instance, natural gasoline. Figure 13 shows an arrangement which has been found satisfactory for entering samples of volatile liquids into the column. All connecting tubing is of very small diameter and as short as possible so that any residual liquid left in the lines, after entering a sample in the column, will not appreciably affect the composition of the comparatively large liquid sample entered. Water in the sample may be frozen out in a U-tube formed from the tubing, as shown, and immersed in a cooling bath held at about −10° C. It is recommended that the pressure in the column be held at about atmospheric while entering liquid samples in order to minimize the effect of any leaks in the connections and valve packing.

The usual method for entering a sample of gasoline or other liquid from the liquid phase at the bottom of the container into the column through such connecting arrangement as described above, introduces no appreciable error when the amount of liquid thus taken out of the sample container is small in relation to the total amount of liquid remaining in the container. On the other hand, if a sample of volatile gasoline, originally almost completely filling its container, is poured out from the liquid phase until only a small fraction of its original volume is left in the container, we may expect an appreciable change in the composition of the gasoline due to the formation of vapor to fill the sample container. In order to determine the limitations within which this method of sampling is sufficiently correct for all practical use, suitable calculations were made on a gasoline composition very easily changed by even slight vaporization.

The gradual removal of liquid from the sample container originally filled 100 per cent is a rather complex process. It may, however, be considered, for purposes of calculation, as a succession of small single flashes (*23*) in each of which a volume of vapor equal to the volume of liquid drained from the container is formed. Thus, the final vapor remaining in the sample container, when the last trace of liquid is drained, is the sum of the contributions of vapor of gradually changing composition yielded by all the single flashes into which the process is divided. This process, it should be pointed out, is not equivalent to simple flashing, as in the case of flashing petroleum heated in a pipe still into a vaporizer, and the changes in composition of liquid and vapor affected by it are not in general the same as by a single flash. Table VI gives the results of the calculations, which should be conservative with regard to the conclusions based on these results.

mol per cent, it is evident that we should not drain more than about half the gasoline in the container. The largest change in composition due to vaporization occurs in the percentage of hexanes and heavier. However, the withdrawal of one-tenth or one-fourth of the liquid in the container effects changes of composition of only a few hundredths of a per cent, which is less than the limits of accuracy usually expected of the method of analysis. With a gallon (3.78-liter) container, successive liquid samples of 60 cc. each are of practically identical composition. For careful work, we should, therefore, use at least one-gallon (3.78-liter) containers almost full of liquid sample (allowing about 5 per cent for outage), and not drain more than half this sample in the process of withdrawing samples for analysis. Within these limitations, it is accurate enough simply to withdraw samples of gasoline from the bottom of the gasoline container as described above.

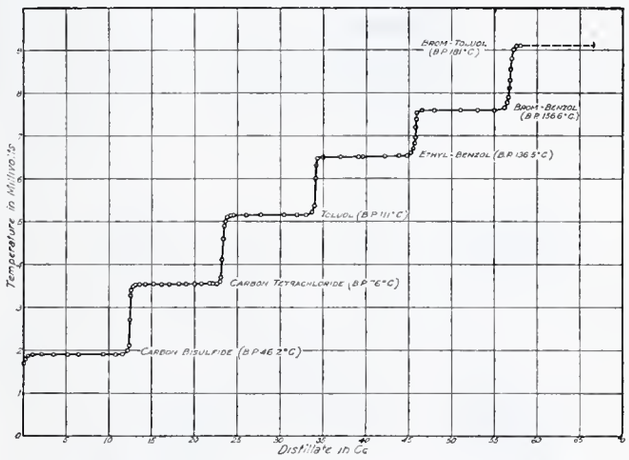


Figure 12—Analysis of Synthetic High-Boiling Mixture Using Modified Precision-Type Column

An optional method for entering gasoline sample into the fractionating column of the apparatus consists in displacement with water under a pressure high enough practically to eliminate the vapor in the sample container (by re-solution in the liquid phase). Since no vaporization of sample occurs, there is no change in composition of the sample even though every bit of it is drained. The use of this sampling method requires sufficient water pressure to insure that all vapor is redissolved in the liquid phase. When this requirement is not met—i. e., when the vapor pressure of the original gasoline equals or exceeds the hydraulic pressure—or when not all the vapor originally present in the sample container can be redissolved (such as any air), highly erratic results may be obtained. The displacement water should be as cold as possible in order to lower the vapor pressure

Table VI—Change in Composition of Natural-Gasoline Sample during Progressive Sampling from Container

Hydrocarbon	Container 100% Full	Container 90% Full	Container 80% Full	Container 70% Full	Container 60% Full	Container 50% Full	Container 40% Full	Container 30% Full	Container 20% Full
	Mol %	*Mol %*	*Mol %*	*Mol %*	*Mol %*	*Mol %*	*Mol %*	*Mol %*	*Mol %*
Ethane	0.20	0.1968	0.1932	0.1893	0.1849	0.1798	0.1739	0.1668	0.1576
Propane	2.0	1.9940	1.9873	1.9797	1.9711	1.9611	1.9491	1.9341	1.9142
Isobutane	8.0	7.9942	7.9878	7.9805	7.9721	7.9624	7.9506	7.9359	7.9161
n-Butane	30.0	29.9908	29.9804	29.9686	29.9553	29.9396	29.9206	29.8967	29.8645
Pentanes	30.0	30.0082	30.0173	30.0276	30.0392	30.0528	30.0690	30.0893	30.1162
Hexanes and heavier	29.80	29.8160	29.8340	29.8543	29.8774	29.9043	29.9368	29.9772	30.0314

This table shows the change in composition of the liquid in the sample container as the container is emptied by gradually draining the liquid. The calculations were not continued beyond 20 per cent liquid in the container, as further calculations would introduce considerable error, due to the re-solution of the mixed vapor formed, in the small remaining amount of liquid. This re-solution effect was not allowed for in the method of computation.

If we expect the method of analysis to check within 0.1

of the gasoline. The gasoline sample is taken off at some suitable point in the container above the highest water level to be carried, but sufficiently below the top of the container to minimize the possibility of sampling any uncondensed vapor which may be trapped at the top of the container. After thus securing and analyzing a sample of gasoline, the vapor pressure of the gasoline at the temperature of the displacement water should be calculated and compared with the hydraulic pressure used. The latter should, of course,

be very much higher. If the reverse is found, this would undoubtedly be owing to the fact that uncondensed and highly volatile vapor was sampled, and not the liquid.

Within their limitations, both methods of sampling are entirely satisfactory. The second method is more accurate, but this is of no practical consequence when less than half the liquid gasoline in a container is drained, as the increased accuracy is greater than that of the method of analysis. The choice of the sampling method will depend, therefore, on circumstances. The limitations and requirements for each method as explained above should be strictly observed.

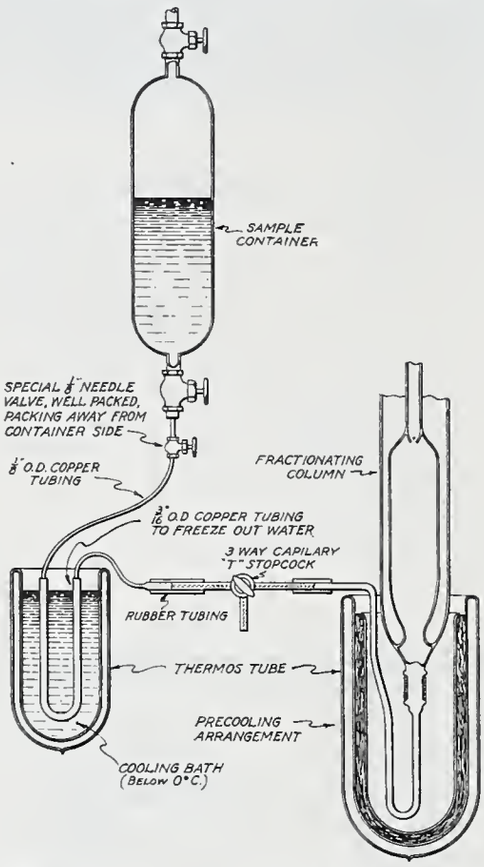


Figure 13—Arrangement for Removing Water from Gasoline Sample before Entering It into Column

Entering Gas Samples into Apparatus—In entering a gas sample into the apparatus, all the usual precautions common to all gas-analysis work should be observed, such as the proper purging of all connecting tubing, avoiding leaks and contamination, etc. When dealing with gases likely to contain heavier hydrocarbons in sufficient quantity to condense out at laboratory temperatures and at atmospheric pressure, it is advisable to displace the sample from the container with hot water and to exert a partial vacuum on the connections between sample container and fractionating column.

Furthermore, since water and carbon dioxide would freeze in the fractionating column and obstruct it, the gas must be passed through a suitable caustic soda or potash trap to remove the carbon dioxide, and through an efficient drying agent, such as phosphorus pentoxide, to remove the water. However, phosphorus pentoxide, when moist, is likely to absorb unsaturated hydrocarbons. Therefore, when a gas sample is likely to contain other than saturated hydrocarbons, some other drying agent must be used, such as magnesium perchlorate trihydrate.

Entering a large gas sample into a fractionating column is likely to require considerable time if reflux cooling alone is resorted to, especially when the gas sample contains a high percentage of methane and lower boiling compounds. Some sort of precooling of the gas sample is therefore advisable. Hitherto, two general methods of precooling gas samples have been used: (A) precooling the gas sample, using a gasoline precooling bath and liquid air as refrigerant; and (B) the total-condensation method, in which practically all of the gas sample (except air and lower boiling compounds) is totally condensed by passing through an external glass bulb immersed directly in liquid air.

Each of these methods has certain advantages and disadvantages over the other. Method A, properly used, requires less time in that the bulk of the methane in the gas sample is vented from the top of the column simultaneously with the entering of the gas sample, instead of condensing all the methane and then slowly distilling it as in method B. Method B is less likely to allow the loss of ethane and heavier as part of the methane fraction; the actual time of entering the gas sample is very short. It might also be mentioned here that in method A a considerable quantity of gasoline bath must be cooled down to low temperatures, requiring considerable quantity of liquid air and constituting a rather inconvenient feature.

Figure 14 illustrates a method of precooling a gas sample which was recently developed in the author's laboratory and is intended to combine the good points of methods A and B without their disadvantages. A tube, shaped somewhat like a large test tube, surrounds the bottom of the fractionating column right up to the vacuum jacket, as shown in the figure. No bath of any kind is used in this tube except, of course, its air content. Liquid air is poured in relatively small quantity into the annular space between the centrally located test tube and the thermos tube. Glass-wool packing distributes liquid air by capillarity over most of the surface of the test tube without actually filling the annular space with the fluid. There is a sufficient drop in temperature between the liquid air and the inside of the precooling tube and heater bulb so that the gas is not completely condensed, as in the total condensation method B; but much more efficient condensation is obtained than with the gasoline-bath method, A, considerable methane being retained in the condensate. Other advantages over the precooling method are: Only a fraction of the liquid air needed to cool a gasoline bath sufficiently is required; the cooling is instantaneous and more efficient. There is very little chance of contact of gasoline with liquid oxygen, as there is a double glass partition. Considerable time is saved in not having to distil a lot of condensed methane as in total-condensation method B.

This same method of radiant precooling will be found helpful in precooling very volatile-liquid samples entered into the liquid column, such as unstabilized natural gasoline.

Accuracy and Checking of Analytical Results—The apparatus, when properly operated, will check itself on duplicate determinations within from a few hundredths of one per cent (see Table IX) to three-tenths or more per cent (*24*), depending on the size of the sample and upon the amount and ease of separation of the component determined. When accurate physical constants are available for interpretation of the analytical results, the absolute accuracy of the results should also run within similar limits. No physical constants or conversion factors are used for the calculation of gas-volume per cents when there is no liquid residue left. The results are therefore free from any inaccuracies in physical constants. A previous article (*24*) discusses in detail various ways in which the general accuracy of this method of analysis has been determined.

It is of great importance to any analyst to be able to check his analytical results from time to time in order to deter-

mine his probable limits of accuracy, and, if the discrepancies thus revealed are excessive, to determine their causes and to remedy them. The most direct and positive method of checking is, of course, to analyze synthetic mixtures with the apparatus and to compare the analytical results with the accurately known composition of the mixture. Unfortunately, the lower boiling hydrocarbons are extremely difficult to prepare in a state of high purity except by using the apparatus to prepare them, which would not, of course, be permissible as a check. There are, however, a number of useful indirect checks, as follows:

(1) Checking (*a*) specific gravity, (*b*) heating value, (*c*) vapor pressure, as calculated from the analysis of the sample, against the experimentally determined values. This check method involves certain assumptions such as ideal gas or solution laws which limit its value. It does, however, furnish a rough check which would reveal larger discrepancies.

(2) Checking on duplicate analyses of the same sample. (See Table IX.) While this constitutes proof of relative and not of absolute accuracy, it is a requirement of any method of analysis.

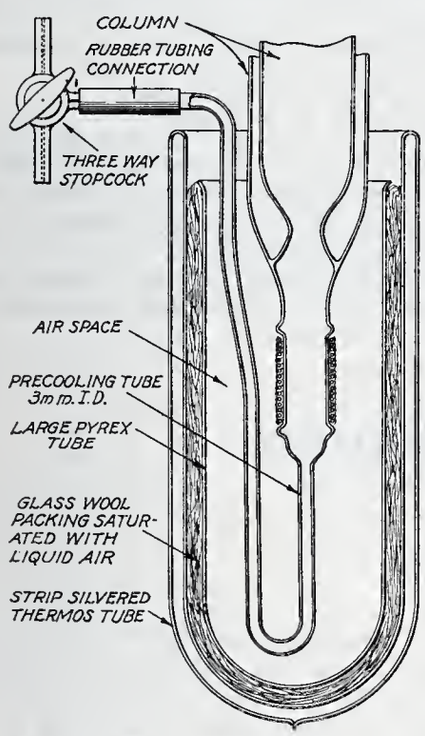


Figure 14—Precooling Arrangement for Gas and Volatile-Liquid Samples

(3) The material-balance method. This method is based on the fact that a pure hydrocarbon is unaffected as to properties and weight by physical processes of vaporization, absorption, and condensation; a material balance may therefore be expected for each hydrocarbon under certain conditions. For instance, two analyzed samples may be mixed in measured proportions and the composite sample analyzed; the analysis of the composite sample should check closely its analysis as calculated from the analysis of the component samples and from their known proportions (Table VII). While not an absolute proof, such a check is evidence that all three analyses are relatively and absolutely correct within the extent of the discrepancies observed. There is, of course, the disadvantage of including the experimental error of mixing the composite sample as an analytical error. A more elaborate and positive check would be obtained by vaporizing a measured and analyzed gasoline sample in a stream of air, analyzing the resulting gasoline-vapor-air mixture and the gasoline residue, and then calculating from the latter two analyses back to the original composition of the gasoline. While this procedure is a very good check on the analyses and on the physical constants used for conversion of gas to liquid and vice versa, it also introduces the possibility of large experimental errors. An elaborate series of analyses resulting in such a material balance is reported by Rogers and Brown (*28*) and discussed by the writer (*24*).

Table VII—Material-Balance Check on Fractional-Distillation Analyses

Hydrocarbon	Gas A	Gas B	Gas C[a] By analysis	Gas C[a] Calcd. from A and B	Gas C[a] Diff.
	%	%	%	%	%
Methane	2.5	76.6	36.36	36.37	−0.01
Ethane	10.9	7.1	8.90	9.16	−0.26
Propane	69.3	7.6	41.30	41.10	+0.20
Isobutane	9.6	1.6	5.34	5.94	−0.60
n-Butane	7.3	3.2	5.83	5.43	+0.40
Pentanes	0.4	1.4	0.99	0.86	+0.13
Hexanes	0.0	1.4	0.69	0.64	+0.05
Heptanes and heavier	0.0	1.1	0.59	0.50	+0.09

[a] Synthetic mixture, 54.3 parts gas A and 45.7 parts gas B.

Checking Fractional-Distillation Analysis against Slow Combustion—The results of a fractional-distillation analysis will not check directly with the results of slow-combustion analysis on the same gas sample. This is, of course, due to the well-known fact that slow combustion can determine a mixture of homologous hydrocarbons only as two equivalent hydrocarbons, and the other hydrocarbons in a sample are determined in terms of these two. It is, however, possible to convert fractional-distillation percentages to percentages that would be obtained by slow combustion on the same sample, using the following equations and analogous ones:

$$1 \text{ volume } C_3H_8 = 2 \text{ volumes } C_2H_6 - 1 \text{ volume } CH_4$$
$$1 \text{ volume } C_4H_{10} = 3 \text{ volumes } C_2H_6 - 2 \text{ volumes } CH_4$$
$$1 \text{ volume } C_5H_{12} = 4 \text{ volumes } C_2H_6 - 3 \text{ volumes } CH_4$$

Note—Equations similar to the above can be made up by noting that two molecules of any hydrocarbon of molecular weight above that of methane are equivalent (as regards behavior in the slow-combustion test) to one molecule of the next lower, plus one molecule of the next higher molecular-weight hydrocarbon, respectively.

For example, a fractional-distillation analysis was converted to a calculated slow-combustion basis by adding twice the propane percentage to the ethane, subtracting once the propane percentage from the methane, thus eliminating propane according to the first equation above, and proceeding in this manner through butane and pentanes and heavier. The gas was also analyzed by actual slow combustion. The comparison is shown in Table VIII.

Table VIII—Correlation of Fractional-Distillation and Slow-Combustion Analyses on Same Sample

Hydrocarbon	Fractional Distillation	Slow Combustion Calcd.	Slow Combustion Actual
	%	%	%
Nitrogen[a]	14.4	14.4	14.4
Oxygen[a]	3.0	3.0	3.0
Methane	72.0	62.8	62.9
Ethane	4.6	19.8	19.7
Propane	3.9		
Isobutane	0.4		
n-Butane	0.8		
Pentanes and heavier	0.9		

[a] Determined by absorption tests.

Table IX—Check Analyses on Gas Sample

Hydrocarbon	Fractional Distillation Run 1	Fractional Distillation Run 2	Fractional Distillation Av.	Slow Combustion Calcd. from av. fractional-distillation analysis	Slow Combustion Actual, propane-and-lighter fraction × 0.9344 Run 1	Slow Combustion Actual Run 2	Slow Combustion Actual Av.
	%	%	%	%	%	%	%
Methane and lighter		34.57	34.57	39.91	39.94	40.05	39.99
Ethane	93.44[b]	10.68	10.68	...	...	...	...
Propane		48.19	48.19	53.53	53.50	53.39	53.45
Isobutane[a]	3.87	3.85	3.86				
n-Butane	2.07	2.09	2.08				
Pentanes and heavier	0.62	0.62	0.62	93.44	93.44	93.44	93.44

[a] Butanes-and-heavier fraction not analyzed owing to difficulty in effecting complete combustion over glowing platinum spiral.

[b] Methane, ethane, and propane not determined separately, owing to difficulty in first part of distillation when a little mercury was accidentally thrown up into column packing where it froze, forming partial obstruction to flow of reflux.

It will be noted that the check is quite close, especially considering that the slow-combustion method, unless very

carefully handled, is itself subject to errors of more than 0.1 or 0.2 per cent.

A more positive check may be obtained by separating a gas sample into two or more fractions using the fractionating column, and then analyzing these fractions by slow-combustion and absorption tests. Table IX shows the check obtained on the propane-and-lighter fraction of a gas sample.

It was found very difficult to effect complete combustion of butane and heavier hydrocarbons, even when the sample was diluted with air and passed into a considerable excess of oxygen. Corrections must be made for deviations from theoretical molecular volumes of the hydrocarbons, as well as of the carbon dioxide formed.

The fractionating efficiency of the column may also be tested by collecting fractions of the supposedly pure hydrocarbons from a fractional distillation, and then analyzing such fractions by slow-combustion and absorption tests. It is, however, well known that a ternary mixture of homologous hydrocarbons, where the component of lowest molecular weight is equal to mol per cent to the one of highest molecular weight, will behave like a pure hydrocarbon in the slow-combustion test. It is, therefore, preferable (1) to divide the sample into strictly binary mixtures (using, of course, the fractionating apparatus) by making cut points in the approximate centers of temperature plateaus where separation is practically perfect, and (2) to analyze the resulting binary mixtures by slow combustion to obtain positive and accurate checks.

The examples given show that close checks can be obtained between the fractional-distillation and the slow-combustion methods of analysis, within the limitations of accuracy of the latter method.

Literature Cited

(1) Allen, Ind. Eng. Chem., Anal. Ed., **1**, 226 (1929).
(2) Burks, *Petroleum World (Los Angeles)*, **13**, No. 9, 102 (1928).
(3) Burrell, Seibert, and Robertson, U. S. Bur. Mines, *Tech. Paper* **104** (1915).
(4) Coffin and Maass, *J. Am. Chem. Soc.*, **50**, 1427 (1928).
(5) Davis, Ind. Eng. Chem., Anal. Ed., **1**, 61 (1929).
(6) Erdman and Stoltzenberg, *Ber.*, **43**, 1702 (1910).
(7) Frey and Yant, Ind. Eng. Chem., **19**, 21 (1927).
(8) Frey and Yant, *Ibid.*, **19**, 492 (1927).
(9) Frey and Yant, *Ibid.*, **19**, 1358 (1927).
(10) Hill, *Petroleum World (Los Angeles)*, **14**, No. 1, 110 (1929).
(11) Kallam, Deckert, and Coulthurst, *Oil Gas J.*, **28**, No. 20, 209 (1929).
(12) Lebeau and Damiens, *Compt. rend.*, **156**, 144, 325, and 797 (1913).
(13) Lucas and Dillon, *J. Am. Chem. Soc.*, **50**, 1460 (1928).
(14) National Standard Petroleum Oil Tables, Bur. Standards, *Circ.* **154** (1924).
(15) Oberfell and Alden, *Oil Gas J.*, **27**, No. 22, 142 (1928).
(16) Podbielniak, Statement contained in partial requirement for degree of University of Michigan Ph.D. Thesis, June, 1928.
(17) Podbielniak, *Petroleum World (Los Angeles)*, **13**, No. 10, 115 (1928).
(18) Podbielniak, *Ibid.*, **13**, No. 11, 99 (1928).
(19) Podbielniak and Gas Analysis Committee of the California Natural Gasoline Assocn., *Ibid.*, **14**, No. 1, 102 (1929).
(20) Podbielniak, *Oil Gas J.*, **27**, No. 35, 38 (1929).
(21) Podbielniak, *Refiner Natural Gasoline Mfr.*, **8**, No. 3, 55 (1929).
(22) Podbielniak, *Oil Gas J.*, **27**, No. 52, 30 (1929).
(23) Podbielniak and Brown, Ind. Eng. Chem., **21**, 773 (1929).
(24) Podbielniak, *Oil Gas J.*, **28**, No. 21, 161 (1929).
(25) Podbielniak, *Ibid.*, **29**, No. 20, 235 (1930).
(26) Robinson, *Ibid.*, **28**, No. 3, 54 (1929).
(27) Robinson, *Natl. Petroleum News*, **21**, No. 44, 181 (1929).
(28) Rogers and Brown, Ind. Eng. Chem., **22**, 258 (1930).
(29) Schaufelberger, *Petroleum World and Oil Age*, p. 73 (Aug., 1930).
(30) Shepherd, *Oil Gas J.*, **28**, No. 6, 48 (1929).
(31) Shepherd and Porter, Ind. Eng. Chem., **15**, 1143 (1923).
(32) Stoltzenberg, *Ber.*, **43**, 1708 (1910).
(33) Travers, "Experimental Study of Gases," p. 211–23, Macmillan, 1901.
(34) Tropsch and Dittrich, *Brennstoff-Chem.*, **6**, 169 (1925).

Detection of Cadmium[1]

J. Stanton Pierce and W. T. Forsee

Georgetown College, Georgetown, Ky.

IN THE standard qualitative tests for ionic cadmium, cupric ion is usually removed with potassium cyanide or iron powder. The potassium cyanide method is the most rapid and, if copper is the only interfering cation, is satisfactory. However, potassium cyanide does not remove traces of other metals which may be present owing to failure to wash out Group III from the precipitate of Group II, or to failure to wash the residue thoroughly in the sodium or ammonium polysulfide extraction, or which may have passed through the filter paper in tests for individual members of Group II-A. Also, particularly for student use in crowded laboratories, potassium cyanide is unsatisfactory, since it is a potential source of prussic acid.

Iron powder satisfactorily removes cupric ion and other interfering cations which may be present, and the ferrous salt formed by the interaction of the iron powder with the above cations does not interfere with the test for cadmium. However, ferrous compounds are readily changed by atmospheric oxygen to ferric, and ferric compounds with an acid solution of hydrogen sulfide, give a precipitate of sulfur, which frequently is mistaken for cadmium sulfide.

Nickel powder has been used successfully to remove interfering cations in the test for cadmium. Nickel powder, if finely divided, readily removes cupric ion from neutral or slightly acid solution, and also removes all other cations tested for in elementary qualitative analysis, which precipitate along with cadmium, with hydrogen sulfide in dilute acid solution. The presence of excess nickel in solution does not interfere with the test for cadmium with hydrogen sulfide.

[1] Received February 9, 1931.

Procedure

To the neutral or slightly acid solution, containing excess sulfate ion, but no acetate, add 1 to 5 grams of fine nickel powder and boil from 3 to 5 minutes. Filter and make a portion of the filtrate 2 *N* in acetic acid. Pass hydrogen sulfide into the acetic acid solution for 15 seconds. A yellow precipitate is cadmium sulfide. A dark precipitate is a sulfide of one of the cations not removed, due to insufficient treatment with nickel, so the remainder of the solution is treated as above.

Test of Method

A mixture containing 100 mg. of cupric ion and 20 mg. each of lead, bismuth, and mercuric ion, and 0.5 mg. of cadmium gave a good test for cadmium by the above procedure on the first filtration, while with the same amounts, except cadmium, no test was obtained.

By increasing the amount of nickel used and the time of boiling the mixture, much larger amounts of interfering elements may be removed. A test for the possible inter-

ference of other elements was made as follows: A mixture was made containing 100 mg. each of the elements, except cadmium, ordinarily tested for in elementary qualitative analysis. The solution was made ammoniacal, just acidified with sulfuric acid, treated with 15 grams of powdered nickel, boiled for 5 minutes, and filtered. The filtrate was made 2 *N* in acetic acid and tested with hydrogen sulfide. A negative test was obtained. With the same amounts of each element mentioned above, and 2 mg. of cadmium, similar treatment gave a distinctly yellow precipitate of cadmium sulfide.

Discussion of Method

By the procedure outlined above, an appreciable amount of cadmium is retained mechanically in the residue of nickel and elements precipitated by nickel. However, as shown by the tests, even though a small amount of cadmium is present initially, enough will be left in the filtrate to give a distinct yellow precipitate with hydrogen sulfide. In this laboratory, the above test for cadmium has been found much more satisfactory in student hands than either of the two standard methods mentioned.

The amount of nickel needed and the time of heating required are determined by the amounts of materials to be removed and the size of the nickel particles. In the experiments described, the nickel powder was 100 mesh or finer.

Lead is the only element listed which is not readily removed with nickel powder and which precipitates along with cadmium in hydrogen sulfide solution 2 *N* in acetic acid. To insure ready removal of lead from solution, excess sulfate is used. This works satisfactorily, if no acetate is present.

Quantitative Determination of Phosgene[1]

J. C. Olsen, George E. Ferguson, Victor J. Sabetta, and Leopold Scheflan

The Polytechnic Institute, Brooklyn, N. Y.

It has been definitely shown that the alcoholic caustic soda method cannot be used to determine phosgene in the thermal decomposition products of carbon tetrachloride mixtures or in samples of phosgene containing other chlorine compounds.

The modified aniline and the sodium iodide–acetone methods have been found to give concordant determinations of phosgene, and are therefore believed to be accurate and trustworthy. Amounts as small as 0.1 mg. may be determined by the acetone method in concentrations of one part per million of air.

The silver nitrate method is not so suitable as either of the preceding methods on account of reduction of the silver nitrate by some of the decomposition products.

In connection with an investigation of the thermal decomposition products of chlorinated hydrocarbons such as carbon tetrachloride, chloroform, etc., it became necessary to determine phosgene in the presence of chlorine, hydrochloric acid, and the chlorinated hydrocarbons originally present, as well as those formed by their thermal decomposition. Several similar investigations had been carried out and the results published (*1, 2, 3, 4*). Various methods of analyzing the gases produced had been employed, in some cases after careful study of the methods available. It soon developed in the present investigation that the methods used in other investigations for the determination of phosgene did not give concordant results. Attempts were made to improve the existing methods with some success.

Previous Methods

The methods which had been used were as follows:

(1) Absorption of the phosgene in alcoholic caustic soda and titration of the excess alkali or determination of the chlorine by some appropriate method. The following reaction takes place:

$$2NaOH + COCl_2 = 2NaCl + CO_2 + H_2O$$

It is obvious that chlorine and hydrochloric acid must be absent.

(2) Absorption of the phosgene in silver nitrate solution to which ammonia has been added in excess of that required to dissolve the precipitate first formed. With this reagent the phosgene decomposes, forming a soluble silver ammonium chloride. On acidifying with nitric acid, the silver chloride is precipitated and may be filtered off and weighed, or the excess silver may be determined by titration. Both chlorine and hydrochloric acid must be absent.

(3) Absorption of the phosgene in a saturated water solution of aniline. Such a solution contains about 26 grams of aniline per liter of water. In this reaction, diphenylurea is formed, when excess of aniline is present, according to the following equation:

$$4C_6H_5NH_2 + COCl_2 = CO(NHC_6H_5)_2 + 2C_6H_5NH_2HCl$$

The diphenylurea is only slightly soluble in water as well as in water saturated with aniline and may be filtered off, washed with cold water, dried at 70° to 80° C., and weighed. This reaction is obviously characteristic of phosgene and would not be brought about by other substances. Hydrochloric acid would interfere only by converting the free aniline into hydrochloride or other compounds. Chlorine would interfere by its oxidizing action upon aniline, producing insoluble compounds.

(4) A method studied and recently published by the German Chemisch-technischen Reichsanstalt consisted in passing the phosgene through a 2 per cent solution of sodium iodide in acetone, and titrating the liberated iodine with standard sodium thiosulfate solution. The following reaction takes place:

$$2NaI + COCl_2 = 2NaCl + I_2 + CO$$

This reaction is quantitative in the absence of water, according to the German Reichsanstalt. Chlorine or any substance capable of liberating iodine from sodium iodide would interfere with the accuracy of this method.

Chlorine may be removed by means of antimony trisulfide or mercuric sulfide, free sulfur and the metallic chlorides being formed. If hydrochloric acid were present, it would react with the antimony sulfide, forming hydrogen sulfide which would react with the iodine liberated in the sodium iodide–acetone solution by the phosgene. Hydrochloric acid has no action upon mercuric sulfide. Hydrochloric acid may be removed by means of zinc dust.

When using the sodium iodide–acetone method for phosgene, all absorbents for chlorine and hydrochloric acid must be free from moisture, which would decompose phosgene. This is accomplished by drying at 110° C. The sodium iodide–acetone solution must also be protected against daylight, which liberates chlorine.

When carbon tetrachloride is decomposed by heat, chlo-

[1] Received December 12, 1930. Presented before the Division of Physical and Inorganic Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

rine, hydrochloric acid, phosgene, and various chlorinated hydrocarbons are formed in varying proportions depending upon the conditions present. The following typical reactions are listed in the report of the German Reichsanstalt:

$$2CCl_4 = C_2Cl_6 + Cl_2 \quad (1)$$
$$2CCl_4 = C_2Cl_4 + 2Cl_2 \quad (2)$$
$$CCl_4 + H_2O = COCl_2 + 2HCl \quad (3)$$
$$CCl_4 + 2H_2O = CO_2 + 4HCl \quad (4)$$
$$2CCl_4 + O_2 = 2COCl_2 + 2Cl_2 \quad (5)$$
$$CCl_4 + O_2 = CO_2 + 2Cl_2 \quad (6)$$
$$CCl_4 + CO_2 = 2COCl_2 \quad (7)$$
$$3CCl_4 + Fe_2O_3 = 3COCl_2 + 2FeCl_3 \quad (8)$$

The decomposition products are, therefore, chlorine, hydrochloric acid, phosgene, carbon dioxide, and chlorinated hydrocarbons. Any attempt to determine the gases chlorine, hydrochloric acid, and phosgene, must also take into account the chlorinated hydrocarbons which are formed during the decomposition of the carbon tetrachloride, or are present in the original fire-extinguishing liquid. Some of these compounds are present in fire-extinguishing liquids such as Pyrene.

Gravimetric and Alcoholic Caustic Soda Methods Discarded

The results of a very extensive investigation of the products obtained by the thermal decomposition of carbon tetrachloride and fire-extinguishing liquids consisting largely of carbon tetrachloride were published in an article by A. C. Fieldner, S. H. Katz, S. P. Kinney, and E. S. Longfellow in October, 1920 (*2*).

These investigators determined the phosgene by passing the gas through a train of reagents containing: (*a*) silver nitrate on granular pumice for removing hydrogen chloride; (*b*) powdered antimony trisulfide for removing chlorine; and (*c*) sodium hydroxide solution in 85 per cent alcohol for the absorption of phosgene, which hydrolyzed to produce sodium chloride.

In the present investigation this method of determining phosgene was compared with the determination by means of aniline and the sodium iodide–acetone method. The phosgene was prepared by the decomposition of carbon tetrachloride, carbon tetrachloride + 10 per cent chloroform, as well as fire-extinguishing liquids consisting mainly of carbon tetrachloride.

The results obtained by absorption in the alcoholic caustic soda solution were found to be much higher than by the aniline and the acetone-iodide method. The determination was carried out both by titrating the chlorine by means of silver nitrate, using potassium chromate as the indicator, and by precipitating and weighing the silver chloride. The results by the titration method were frequently higher than those obtained by weighing the silver chloride. In carrying out the titration, the caustic soda was first acidified by means of nitric acid and then neutralized by the addition of sodium bicarbonate, but the alcohol was not expelled. Difficulty was experienced in titration on account of reduction of the silver nitrate.

Believing that the reduction was caused by the alcohol present, the solution was evaporated nearly to dryness after neutralization with nitric acid and sodium bicarbonate, both for the titration and weighing the silver chloride. The titration results continued to be high, and, in fact, were high even when the silver chloride was filtered off and weighed from the same solution which had been titrated.

In a further study of this method, it was found that the alcoholic caustic soda solution through which the carbon tetrachloride had been passed turned dark brown on standing overnight, clearly indicating decomposition of the carbon tetrachloride. A silver mirror was also formed on heating the solution. When the solution which had been acidified with nitric acid and evaporated to expel the alcohol was neutralized and treated with silver nitrate, a yellow precipitate was formed which dissolved in nitric acid leaving white silver chloride. The silver chloride is undoubtedly formed from the hydrolysis of carbon tetrachloride, which is soluble in the alcoholic caustic soda solution. The dark color which develops on standing would indicate that other decomposition products are also formed.

Several experiments were then carried out in which the carbon tetrachloride was volatilized and passed through the alcoholic caustic soda solution without heating. Under these conditions no phosgene could be present. In these experiments considerable quantities of chlorides were found by titration and weighing silver chloride.

These reactions are believed to account for the high values obtained by titration as compared with the gravimetric determination of silver chloride.

The gravimetric method, when used to determine phosgene produced by the thermal decomposition of carbon tetrachloride and similar compounds, would give high results on account of the hydrolysis of carbon tetrachloride and other chlorinated hydrocarbons.

As this method was used by Fieldner and his associates, this source of error must have given high results in their experiments.

The alcoholic caustic soda method has been very largely used to determine phosgene when diluted with air alone. Our experiments indicate that phosgene is frequently accompanied by chlorine compounds other than phosgene which tend to give high results for phosgene when this method is used.

Experiments Using Acetone and Aniline Methods

A great many determinations of phosgene by means of the acetone and aniline methods gave quite uniformly higher results by the acetone than by the aniline method. The aniline method, being a gravimetric method, would be influenced by the solubility of the precipitated diphenylurea. This compound was known to be slightly soluble in water. A determination of its solubility in the saturated aniline water used gave 5.5 mg. diphenylurea in 100 cc. of saturated aniline solution.

In order to overcome this error, the aniline water used was saturated with diphenylurea by passing phosgene into the solution until a small amount of precipitate was formed which was filtered off, the clear filtrate being used for the phosgene determinations. Using 75 cc. of the aniline solution, the solution saturated with diphenylurea gave, in four determinations, 4.6, 7.5, 3.4, and 3.5 mg. of phosgene more than was obtained from the aniline solution unsaturated with the precipitate. When saturating the aniline solution by passing phosgene, evidence of the solubility of the precipitate could readily be observed by noting the amount of gas passed in before a permanent precipitate was obtained. A similar observation was often made in making comparative tests for phosgene with the acetone-iodide method.

The use of the aniline solution saturated with diphenylurea undoubtedly gives more accurate quantitative results and makes this method more delicate, so that lower concentrations of phosgene may be detected and determined.

Tests were also carried out to ascertain the optimum time necessary for complete precipitation of the diphenylurea. The aniline solution containing the precipitate was allowed to stand 2 hours before filtering, duplicate determinations being allowed to stand overnight. The solution which stood

for 2 hours gave higher results than the one standing overnight, the differences being 1.5 and 2.2 mg. The diphenylurea evidently is slowly decomposed.

The precipitate is filtered on a Gooch crucible, washed with a small amount of the filtrate, and dried at 70° to 80° C. Precipitates dried to constant weight at this temperature lost weight when heated to 100° C. Instead of washing with cold water, it was found equally satisfactory to volatilize the excess aniline by means of sucking air through the Gooch.

The acetone method in a great many determinations gave results considerably higher than the aniline method. By drying the gases with calcium chloride, results of much better agreement were obtained. In a series of about twenty determinations in which the acetone method was compared with the aniline method using the saturated aniline solution, differences of only a few milligrams of phosgene were obtained between the two methods, the acetone method generally giving the higher result. The acetone method gives indication of very small amounts of phosgene by the reddish yellow color of the liberated iodine. Fiftieth or one hundredth normal sodium thiosulfate solution was used to titrate these small amounts of iodine. The usual starch indicator cannot be used in the acetone solution, but the color of the iodine affords a fairly sharp end point. The yellow color returns slowly on standing.

When the aniline solution saturated with diphenylurea was used, traces of phosgene could be detected by the appearance of a slight turbidity. The filtration and weighing of such slight precipitates could not be carried out as accurately as the titration of the iodine in the acetone solution.

Silver Nitrate Method Discarded

A number of determinations of phosgene were made which indicated that the silver nitrate method gave results very close to the true value. In using this method, the silver chloride was precipitated and weighed. Titration of the excess of silver was not found to be feasible because a considerable amount of silver was reduced, presumably by unsaturated hydrocarbons present in the gas mixture.

Accuracy of Methods Tested and Modification Adopted

The attempt was made to check the accuracy of these methods by using known amounts of pure phosgene. A sample of the purest liquid phosgene available at Edgewood Arsenal was obtained for this purpose. A steel cylinder was used as the container. By connecting the cylinder to a gas buret filled with dry clean mercury, it was found possible to transfer to the buret any desired amount of phosgene. As the boiling point of pure phosgene at atmospheric pressure is 8.3° C., the liquid readily volatilized at room temperature and passed into the buret. The gas is sufficiently stable to give constant volumetric readings over mercury. After reading the volume and noting the temperature and pressure, the gas was usually diluted to 100 cc. with dry air. Care was taken in making the readings of the phosgene to wait until the reading was constant. No difficulty was experienced in this respect, and no change was noted in the volume of the gas before dilution with air.

The volume of gas obtained in this manner was passed through the absorbing solution, any remaining phosgene in the buret and tubes being swept out by means of air.

The results obtained in this manner were low when calculated on the assumption that the gas obtained was pure. As the experiments progressed, the differences became greater. This seemed to indicate that some decomposition was taking place in the phosgene.

Experiments in which the phosgene was absorbed showed that there was some gas which was not taken up by water saturated with aniline. The cylinder containing the phosgene was then connected with a manometer and the temperature of the phosgene cylinder reduced to the boiling point of phosgene—namely, 8.3° C. At this temperature, the pressure in the cylinder was some 14 inches (35.56 cm.) higher than atmospheric pressure. The cylinder was then placed in a refrigerator, cooled very much below the boiling point, and again placed in a bath of cold water until the temperature seemed to be constant at 8.3° C. The pressure reading was even then very high.

Under these conditions it did not seem possible that the gas obtained from this cylinder was pure phosgene gas.

In a further attempt to check the method of analysis for the pure phosgene, a sample of phosgene dissolved in toluene was obtained. Samples of gas were drawn from this flask in a manner similar to that used with the cylinder of liquid phosgene, except that the flask was placed in water warmed to 35° to 40° C. The following results were obtained from this gas:

Acetone Method	Aniline Method
35.25	35.99
35.10	35.78
Av. 35.18	Av. 35.88

These results show very excellent checks with the two methods, with a slightly higher result with the aniline method.

A second sample of phosgene dissolved in toluene was obtained and tested. A considerable number of determinations of the gas obtained from this sample were made by the acetone, aniline, and alcoholic caustic method, the average of all the results obtained being as follows: acetone, 36.72 per cent; aniline, 36.68 per cent; caustic soda, 58.92 per cent. Two absorption bottles were used with each reagent, only traces being found in every case in the second absorption liquid. This indicates that all three reagents are very efficient absorbents of phosgene.

In the endeavor to ascertain why such high results were obtained with the caustic soda reagent, absorption trains were arranged with aniline water followed by the soda reagent, and another train with the acetone reagent followed by the soda reagent. In both cases considerable amounts of chlorine were found in the soda reagent. This shows that there are chlorine compounds in the phosgene being tested which are not phosgene. This accounts for the high results obtained with the soda reagent.

This conclusion was further confirmed by a determination of the chlorine present in the filtrate from the diphenylurea. This was found to be higher than the amount of chlorine corresponding to the phosgene present as shown by the weight of diphenylurea. In two determinations the amount was 8.48 and 7.96 per cent after deducting the result of the blank determination.

The gas obtained from phosgene dissolved in toluene is therefore not pure phosgene but contains other chlorine compounds. The close agreement of the results obtained by two such dissimilar methods as aniline and acetone solution of sodium iodide would indicate that these reagents give the true percentage of phosgene.

Literature Cited

(1) Biesalski, E., *Z. angew. Chem.*, **37**, 314 (1924).
(2) Fieldner, A. C., Katz, S. H., Kinney, S. P., and Longfellow, E. S., *J. Franklin Inst.*, **190**, 543 (1920).
(3) Jahresbericht der Chemisch-technischen Reichsanstalt, Vol. V, pp. 11–20 (1926).
(4) *Ibid.*, Vol. VI, pp. 57–63 (1927).

Interpretation of Water Analysis

Equilibrium Considerations Determining Activities and Concentrations of Ions[1]

D. S. McKinney

Power Stations Department, Duquesne Light Co., Pittsburgh, Pa.

Defects in the methods now in use for determining the alkaline ions in water are pointed out.

Two methods of calculating the anions of carbonic and orthophosphoric acids are presented in which the relations between the pH value, the dissociation constants of these acids, and the dissociation constant of water are used to calculate the concentrations of the various alkaline ions at 25° C.

The more accurate method utilizes the simplified Hückel and Debye equation to calculate the ion concentrations from the ion activities, and requires complete analysis of the water.

The less accurate method assumes that ion activities and concentrations are equal, and requires the determination of pH, total phosphate, and a titration from pH 5.0 to pH 8.5.

Tables are presented which reduce the calculations to simple arithmetic, and the method of calculation is illustrated by an example. The need for data at high temperatures is indicated.

Introduction[2]

It is an interesting observation that the results of studies of the physical chemistry of dilute aqueous solutions have found meager applications to the analytical and applied chemistry of industrial water supplies. Methods of analysis, stoichiometric in character, and developed primarily for the examination of concentrated solutions, have been and still are applied to the examination of industrial waters. These methods are employed to obtain data from which it is attempted to interpret the mechanism of corrosion and scale formation, and for the conditioning of water to prevent corrosion and scale formation.

The customary methods are those prepared jointly by the American Chemical Society and the American Public Health Association, and published by the latter as standard methods. These have been used for lack of more appropriate ones, for the complete analyses of natural, conditioned (chemically and thermally), and concentrated boiler waters. They have been used in the field for control of conditioning systems, and other studies. Inconsistencies have been observed in the results obtained, not wholly explained by lack of accuracy in the analytical procedure. For example, in the complete analyses of water, apparently containing bicarbonate, the content of this anion appeared materially in excess of the sum of the cations. In distilled water, the inclusion of the determined bicarbonate completely upsets the analysis. No hydroxide was registered in boiler waters treated with trisodium phosphate, although the pH value was in excess of 9.0.

The application of some studies of the physical chemistry of dilute aqueous solutions was prompted by an attempt to explain the apparent confusion resulting from the use of existing methods. It was further believed that the relation existing between the H-ion concentration of a water and the quantities of ions present could be utilized in the control and treatment of concentrated water and would provide data for use in a more rational explanation of corrosion phenomena occurring in the steam and water cycle. A further purpose of the study by the author was a more exact evaluation of free carbon dioxide and the anions which produce alkalinity in water. It is apparent from the following development of the application of ion activities that a new procedure is available for the conditioning of water for both scale prevention and inhibition of corrosion.

The pH determination has been considered as a separate item in the usual water analysis. As will be noted in the discussion, the relation of the H-ion concentration of the water and the quantities of the ions present is necessary.

If the stoichiometric methods of analysis now in use fail to evaluate correctly the concentration of the weakly dissociated acids in water, it must be concluded that the interpretations of the data are erroneous. Water technologists need, then, to recognize the application of physical chemistry to the chemistry of water if the evaporative industries are to avoid economic losses, the results of corrosion, and scale formation.

General Considerations

The determination of the correct ion concentration and activities in water is necessary in industrial processes to prevent corrosion and the formation of deposits. The ion concentrations determine the possible quantity of metal corroded, of deposit formed, and of reagents required to produce a given amount of desired precipitate. The ion activities determine corrosion rates (except as modified by the use of inhibitors or by the phenomenon of passivity), the character of deposit which will precipitate from a particular water, and the amount of excess reagent required to produce a desired precipitate.

Present methods of determining the anions of the slightly dissociated acids (carbonic and phosphoric and their salts) are stoichiometric, and disregard the equilibria which control the relations of these anions and of hydrogen and hydroxyl ions. Therefore, they give the operator a false impression of the quantities of each anion present. For example, a dilute solution of sodium carbonate is considered, stoichiometrically, to contain only the carbonate anion. The pH value of such a solution is approximately 11. Hence, from equilibrium considerations, the hydroxyl-ion concentration must be that required by the equilibrium constant of water, and the relation of carbonate to bicarbonate ion must be that required by the second dissociation constant of carbonic acid at this pH value.

Further, the results obtained by present methods cannot be evaluated when more than one weak acid is present unless unwarranted assumptions are made. For example, in mixtures of silicate and carbonate compounds, the assumption that the silicate is present as silicon dioxide, or in the case of mixtures of phosphate and carbonate compounds, the assumption that the phosphate is present as phosphate (by some operators HPO^{4--}).

[1] Received December 19, 1930.

[2] By Max Hecht, Power Stations Department, Duquesne Light Company.

Derivation of Formulas

A method and tables for the calculation of the activities and concentrations of the ions of carbonic and orthophosphoric acids at 25° C. is outlined. This method may be applied to any other weak acids, if their dissociation constants are known. The data obtained below are applicable only to the treatment of water at room temperature. The method, however, is applicable to the treatment of water at any temperature if the necessary constants are known at the desired temperature.

In the following, a represents molal activity—i. e., the limit of the molality (c) as the total concentration approaches zero equals the activity.

Carbonic acid dissociates as follows:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

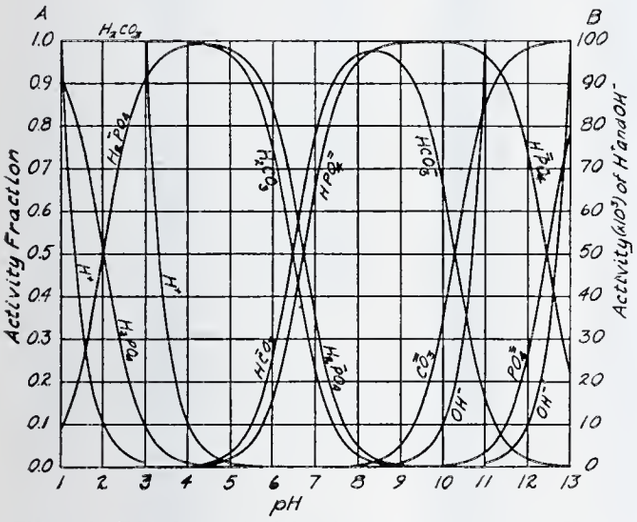


Figure 1—Relation of Activity Fractions of Anions of H_2CO_3 and H_3PO_4, and Activity ($\times 10^3$) of H^+ and OH^- to pH

(Read scale A for all values except activity of H^+ at pH 1 to 3, and OH^- at pH 11 to 13)

From the law of mass action

$$K_1 = \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{H_2CO_3}} \text{ or } \frac{K_1}{a_{H^+}} = \frac{a_{HCO_3^-}}{a_{H_2CO_3}}$$

$$\text{and } K_2 = \frac{a_{H^+} \cdot a_{CO_3^{--}}}{a_{HCO_3^-}} \text{ or } \frac{K_2}{a_{H^+}} = \frac{a_{CO_3^{--}}}{a_{HCO_3^-}}$$

The dissociation constants of carbonic acid (*3*) are

$$K_1 = 3.5 \times 10^{-7} \text{ and } K_2 = 5.4 \times 10^{-11}$$

Note—Walker, Bray, and Johnston [*J. Am. Chem. Soc.*, **49**, 1235 (1927)] obtain $K_2 = 3.85 \times 10^{-11}$. Since an error of only 0.025 in the pH value will produce a difference equal to that between the two values for K_2, and industrial measurements are seldom made with this accuracy, Tables I and II have not been recalculated.

These relations may be expressed

$$a_{H_2CO_3} : a_{HCO_3^-} : a_{CO_3^{--}} = 1 : \frac{K_1}{a_{H^+}} : \frac{K_1 \cdot K_2}{a^2_{H^+}}$$
$$= 1 : \frac{3.5 \cdot 10^{-7}}{a_{H^+}} : \frac{1.89 \cdot 10^{-17}}{a^2_{H^+}} \qquad (1)$$

$$\text{Let } x = \text{pH} = \log \frac{1}{a_{H^+}}; \text{ then } a_{H^+} = 10^{-x}$$

Substituting 10^{-x} for a_{H^+} in proportion (1) we obtain

$$a_{H_2CO_3} : a_{HCO_3^-} : a_{CO_3^{--}} = 1 : 3.5 \cdot 10^{(x-7)} : 1.89 \cdot 10^{(2x-17)}$$

Proceeding in a like manner for orthophosphoric acid, whose dissociation constants (*4*) are

$$K_1 = 10^{-2},\ K_2 = 1.95 \times 10^{-7}, \text{ and } K_3 = 3.6 \times 10^{-13}$$

we obtain,

$$a_{H_3PO_4} : a_{H_2PO_4^-} : a_{HPO_4^{--}} : a_{PO_4^{---}} = 1 : \frac{K_1}{a_{H^+}} : \frac{K_1 \cdot K_2}{a^2_{H^+}} : \frac{K_1 \cdot K_2 \cdot K_3}{a^3_{H^+}}$$
$$= 1 : 10^{(x-2)} : 1.95 \cdot 10^{(2x-9)} : 7.02 \cdot 10^{(3x-22)}$$

Also

$$a_{H^+} \cdot a_{OH^-} = K_w = 10^{-14}$$

Hence, since

$$a_{H^+} = 10^{-x},\ a_{OH} = 10^{(x-14)}$$

If we let

$$a_{H_2CO_3} + a_{HCO_3^-} + a_{CO_3^{--}} = a_C \text{ and } a_{H_3PO_4} + a_{H_2PO_4^-} + a_{HPO_4^{--}} + a_{PO_4^{---}} = a_P$$

the formulas of Table I may be obtained.

The fractional activity of each ion may be calculated from the formulas of Table I. These fractions have been calculated for each 0.1 pH from a pH of 1 to a pH of 13, and are given together with the activities of hydrogen and hydroxyl in Table II. Linear interpolation between these values will be sufficiently accurate for the purposes of water analysis. The data of Table II are shown graphically in Figure 1.

Table I—Formulas for Activity Ratios

pH = x

$$\frac{a_{H_2CO_3}}{a_C} = \frac{1}{1 + 3.5 \cdot 10^{(x-7)} + 1.89 \cdot 10^{(2x-17)}} = \frac{1}{1 + 10^{(x-6.456)} + 10^{(2x-16.724)}}$$

$$\frac{a_{HCO_3^-}}{a_C} = \frac{3.5.10^{(x-7)}}{1 + 3.5 \cdot 10^{(x-7)} + 1.89 \cdot 10^{(2x-17)}} = \frac{10^{(x-6.456)}}{1 + 10^{(x-6.456)} + 10^{(2x-16.724)}}$$

$$\frac{a_{CO_3^{--}}}{a_C} = \frac{1.89 \cdot 10^{(2x-17)}}{1 + 3.5 \cdot 10^{(x-7)} + 1.89 \cdot 10^{(2x-17)}} = \frac{10^{(2x-16.724)}}{1 + 10^{(x-6.456)} + 10^{(2x-16.724)}}$$

$$\frac{a_{H_3PO_4}}{a_P} = \frac{1}{1 + 10^{(x-2)} + 1.95 \cdot 10^{(2x-9)} + 7.02 \cdot 10^{(3x-22)}} = \frac{1}{1 + 10^{(x-2)} + 10^{(2x-8.710)} + 10^{(3x-21.154)}}$$

$$\frac{a_{H_2PO_4^-}}{a_P} = \frac{10^{(x-2)}}{1 + 10^{(x-2)} + 1.95 \cdot 10^{(2x-9)} + 7.02 \cdot 10^{(3x-22)}} = \frac{10^{(x-2)}}{1 + 10^{(x-2)} + 10^{(2x-8.710)} + 10^{(3x-21.154)}}$$

$$\frac{a_{HPO_4^{--}}}{a_P} = \frac{1.95 \cdot 10^{(2x-9)}}{1 + 10^{(x-2)} + 1.95 \cdot 10^{(2x-9)} + 7.02 \cdot 10^{(3x-22)}} = \frac{10^{(2x-8.710)}}{1 + 10^{(x-2)} + 10^{(2x-8.710)} + 10^{(3x-21.154)}}$$

$$\frac{a_{PO_4^{---}}}{a_P} = \frac{7.02 \cdot 10^{(3x-22)}}{1 + 10^{(x-2)} + 1.95 \cdot 10^{(2x-9)} + 7.02 \cdot 10^{(3x-22)}} = \frac{10^{(3x-21.154)}}{1 + 10^{(x-2)} + 10^{(2x-8.710)} + 10^{(3x-21.154)}} =$$

$$a_{H^+} \cdot 10^3 = 10^{(3-x)} \qquad a_{OH} \cdot 10^3 = 10^{(x-11)}$$

USEFUL FACTORS

	f_1	f_2		f_1	f_2
Fe^{++}	0.03582	27.92	CO_3^{--}	0.03333	30.00
Al^{+++}	0.1112	8.99	H_3PO_4 *b*	0.01020	98.05
Ca^{++}	0.04990	20.04	$H_2PO_4^-$	0.01031	97.04
Mg^{++}	0.08224	12.16	HPO_4^{--}	0.02082	48.02
Na^+	0.04348	23.00	PO_4^{---}	0.03157	31.68
K^+	0.02558	39.096	SO_4^{--}	0.02082	48.03
H^+	0.9921	1.008	Cl^-	0.02820	35.46
OH^-	0.05880	17.008	NO_3^-	0.01613	62.01
CO_2 *b*	0.02273	44.00	NO_2^-	0.02173	46.01
HCO_3^-	0.01639	61.01			

P. p. m. $\times f_1$ = milliequivalents per liter. Milliequivalents per liter $\times f_2$ = p. p. m. *b* P. p. m. $\times f_1$ = millimols per liter. Millimols per liter $\times f_2$ = p. p. m. Millimols $\times$ valence = milliequivalents.

A study of the above will show that the pH value determines the activities of hydrogen and hydroxyl and the ratios of the activities of the various ions of carbonic and phosphoric acids. In order to obtain the ion concentrations and activities, it is necessary to know the activity coefficient. The relation between the activity and the concentration may be expressed:

Table II—Activity Fractions—H_3PO_4, H_2CO_3, and H_2O for Phosphoric and Carbonic Acids and Water

pH	$\frac{a_{H_3PO_4}}{a_P}$	$\frac{a_{H_2PO_4^-}}{a_P}$	$\frac{a_{HPO_4^{--}}}{a_P}$	$\frac{a_{PO_4^{---}}}{a_P}$	$\frac{a_{H_2CO_3}}{a_C}$	$\frac{a_{HCO_3^-}}{a_C}$	$\frac{a_{CO_3^{--}}}{a_C}$	$a_{H^+}\cdot 10^3$	$a_{OH^-}\cdot 10^3$
1.0	0.9091	0.0909	0.0000	0.0000	1.0000	0.0000	0.0000	100.00	0.0000
1.1	0.8882	0.1118			1.0000			79.44	
1.2	0.8632	0.1368			1.0000			63.10	
1.3	0.8337	0.1663			1.0000			50.12	
1.4	0.7992	0.2008			1.0000			39.81	
1.5	0.7598	0.2402			1.0000			31.62	
1.6	0.7153	0.2847			1.0000			25.12	
1.7	0.6661	0.3339			1.0000			19.95	
1.8	0.6131	0.3869			1.0000			15.85	
1.9	0.5573	0.4427			1.0000			12.30	
2.0	0.5000	0.5000			1.0000			10.00	
2.1	0.4427	0.5573			1.0000			7.944	
2.2	0.3868	0.6132			1.0000	0.0000		6.310	
2.3	0.3339	0.6661			0.9999	0.0001		5.012	
2.4	0.2847	0.7153			0.9999	0.0001		3.981	
2.5	0.2403	0.7597	0.0000		0.9999	0.0001		3.162	
2.6	0.2008	0.7991	0.0001		0.9999	0.0001		2.512	
2.7	0.1663	0.8336	0.0001		0.9998	0.0002		1.995	
2.8	0.1368	0.8631	0.0001		0.9998	0.0002		1.585	
2.9	0.1118	0.8881	0.0001		0.9997	0.0003		1.230	
3.0	0.0909	0.9089	0.0002		0.9997	0.0003		1.000	
3.1	0.0736	0.9262	0.0002		0.9996	0.0004		0.7944	
3.2	0.0593	0.9404	0.0003		0.9994	0.0006		0.6310	
3.3	0.0477	0.9519	0.0004		0.9993	0.0007		0.5012	
3.4	0.0383	0.9612	0.0005		0.9991	0.0009		0.3981	
3.5	0.0306	0.9688	0.0006		0.9989	0.0011		0.3162	
3.6	0.0245	0.9747	0.0008		0.9986	0.0014		0.2512	
3.7	0.0195	0.9795	0.0010		0.9983	0.0017		0.1995	
3.8	0.0156	0.9832	0.0012		0.9978	0.0022		0.1585	
3.9	0.0124	0.9861	0.0015		0.9972	0.0028		0.1230	
4.0	0.0099	0.9882	0.0019		0.9965	0.0035		0.1000	
4.1	0.0079	0.9897	0.0024		0.9956	0.0044		0.0794	
4.2	0.0063	0.9906	0.0031		0.9945	0.0055		0.0631	
4.3	0.0050	0.9911	0.0039		0.9931	0.0069		0.0512	
4.4	0.0039	0.9912	0.0049		0.9913	0.0087		0.0398	
4.5	0.0031	0.9908	0.0061		0.9890	0.0110		0.0316	
4.6	0.0025	0.9898	0.0077		0.9863	0.0137		0.0251	
4.7	0.0020	0.9883	0.0097		0.9828	0.0172		0.0200	
4.8	0.0016	0.9863	0.0121		0.9784	0.0216		0.0159	
4.9	0.0012	0.9836	0.0152		0.9730	0.0270		0.0123	
5.0	0.0010	0.9799	0.0191		0.9662	0.0338		0.0100	
5.1	0.0008	0.9753	0.0239		0.9577	0.0423		0.0079	
5.2	0.0006	0.9694	0.0300		0.9475	0.0525		0.0063	
5.3	0.0005	0.9621	0.0374		0.9347	0.0653		0.0050	
5.4	0.0004	0.9529	0.0467		0.9192	0.0808		0.0040	
5.5	0.0003	0.9416	0.0581		0.9003	0.0997		0.0032	
5.6	0.0002	0.9278	0.0720		0.8777	0.1223		0.0025	
5.7	0.0002	0.9108	0.0890		0.8508	0.1492		0.0020	
5.8	0.0001	0.8903	0.1095		0.8191	0.1809		0.0016	
5.9	0.0001	0.8658	0.1341		0.7825	0.2175		0.0012	
6.0	0.0001	0.8368	0.1632		0.7408	0.2592		0.0010	
6.1	0.0001	0.8028	0.1971		0.6942	0.3058		0.0008	
6.2	0.0000	0.7639	0.2361		0.6433	0.3567		0.0006	
6.3		0.7199	0.2801		0.5889	0.4111	0.0000	0.0005	
6.4		0.6713	0.3287		0.5321	0.4678	0.0001	0.0004	
6.5		0.6186	0.3814		0.4746	0.5253	0.0001	0.0003	0.0000
6.6		0.5630	0.4370		0.4178	0.5821	0.0001	0.0003	0.0000
6.7		0.5058	0.4942		0.3630	0.6368	0.0002	0.0002	0.0001
6.8		0.4484	0.5516		0.3116	0.6882	0.0002	0.0002	0.0001
6.9		0.3924	0.6076		0.2645	0.7352	0.0003	0.0001	0.0001
7.0		0.3390	0.6610		0.2222	0.7774	0.0004	0.0001	0.0001

$$a = \alpha c$$

where a = activity
α = activity coefficient
c = concentration (molality)

This coefficient may be obtained by calculation from the complete water analysis by means of the simplified equation of Debye and Hückel as modified by Noyes (*5*).

$$\log \alpha = -0.298\nu^2\sqrt{\Sigma c\nu^2}$$

where α = activity coefficient
ν = valence of ion considered
$\Sigma\nu c^2$ = sum of products of individual ion concentrations (molality) multiplied by squares of their valences.

Values of α calculated by this equation may be read from Figure 2, in which α is plotted against $\Sigma c\nu^2$ for mono-, bi-, and tri-valent ions. If the total concentration of the carbonate compounds is known, ion concentrations may be selected whose sum equals the total concentration, and which, when multiplied by the corresponding activity coefficients, lead to activities whose ratio to one another corresponds to those given in Table II for the particular pH. The ion concentrations of phosphoric acid are calculated in the same way as the carbonate.

In case the concentrations are so low that the activity coefficient of the ions considered are equal, the activity ratios will be equal to the concentration ratios and the concentrations may be very easily calculated. A clear understanding of the method of calculation may be obtained from the examples which follow:

Application of Formulas

When maximum accuracy is desired, the requirements for the calculations are complete analysis of the water, including pH value, total carbon dioxide, and total phosphate, regardless of the form of combination.

For routine work, where less accuracy is necessary, the requirements are pH value, total phosphate, and amount of acid necessary to titrate the water, preferably from pH 8.5 to pH 5.

Three samples of synthetic water were prepared from 0.1 *M* solution of the necessary reagents. Sample 1 represents a boiler water formed by the distillation of lime-soda or zeolite-treated water; sample 2 represents a boiler water in which phosphates are used; and sample 3 represents a raw water.

Table III—Results of Test of Synthetic Water

Reagent (c. p.)	Concentration of Reagent in Solution		
	Sample 1 *Millimols/liter*	Sample 2 *Millimols/liter*	Sample 3 *Millimols/liter*
Na_2CO_3	1.000	1.000	0.500 ($NaHCO_3$)
NaOH	8.000	6.000	0
KH_2PO_4	0	1.000	0
Na_2SO_4	7.000	3.000	0.500
NaCl	5.000	1.000	0.400
HCl	0	0	0.300

Table II—Activity Fractions—H_3PO_4, H_2CO_3, and H_2O for Phosphoric and Carbonic Acids and Water *(Continued)*

pH	$\frac{a_{H_3PO_4}}{a_P}$	$\frac{a_{H_2PO_4^-}}{a_P}$	$\frac{a_{HPO_4^{--}}}{a_P}$	$\frac{a_{PO_4^{---}}}{a_P}$	$\frac{a_{H_2CO_4}}{a_C}$	$\frac{a_{HCO_4^-}}{a_C}$	$\frac{a_{CO_3^{--}}}{a_C}$	$a_{H^+}\cdot 10^3$	$a_{OH^-}\cdot 10^3$
7.1		0.2895	0.7105		0.1849	0.8146	0.0005	0.0001	0.0001
7.2		0.2445	0.7555		0.1527	0.8466	0.0007	0.0001	0.0002
7.3		0.2045	0.7955		0.1252	0.8739	0.0009	0.0001	0.0002
7.4		0.1696	0.8304		0.1020	0.8968	0.0012	0.0000	0.0003
7.5		0.1395	0.8605		0.0827	0.9157	0.0016		0.0003
7.6		0.1141	0.8859		0.0668	0.9312	0.0020		0.0004
7.7		0.0928	0.9072		0.0538	0.9436	0.0026		0.0005
7.8		0.0752	0.9248		0.0432	0.9535	0.0032		0.0006
7.9		0.0607	0.9393		0.0346	0.9613	0.0041		0.0008
8.0		0.0488	0.9512		0.0276	0.9672	0.0052		0.0010
8.1		0.0391	0.9609	0.0000	0.0220	0.9714	0.0066		0.0012
8.2		0.0313	0.9686	0.0001	0.0176	0.9741	0.0083		0.0016
8.3		0.0251	0.9748	0.0001	0.0140	0.9755	0.0105		0.0020
8.4		0.0200	0.9799	0.0001	0.0111	0.9757	0.0132		0.0025
8.5		0.0160	0.9839	0.0001	0.0088	0.9746	0.0166		0.0032
8.6		0.0127	0.9872	0.0001	0.0070	0.9721	0.0209		0.0040
8.7		0.0101	0.9897	0.0002	0.0055	0.9683	0.0262		0.0050
8.8		0.0081	0.9917	0.0002	0.0044	0.9628	0.0328		0.0063
8.9		0.0064	0.9933	0.0003	0.0034	0.9557	0.0409		0.0079
9.0		0.0051	0.9945	0.0004	0.0027	0.9462	0.0511		0.0100
9.1		0.0041	0.9954	0.0005	0.0021	0.9344	0.0635		0.0123
9.2		0.0032	0.9962	0.0006	0.0017	0.9197	0.0786		0.0159
9.3		0.0026	0.9967	0.0007	0.0013	0.9016	0.0971		0.0200
9.4		0.0020	0.9971	0.0009	0.0010	0.8798	0.1192		0.0251
9.5		0.0016	0.9973	0.0011	0.0008	0.8536	0.1456		0.0316
9.6		0.0013	0.9973	0.0014	0.0006	0.8227	0.1767		0.0398
9.7		0.0010	0.9972	0.0018	0.0004	0.7869	0.2127		0.0512
9.8		0.0008	0.9969	0.0023	0.0003	0.7458	0.2539		0.0631
9.9		0.0006	0.9966	0.0028	0.0003	0.7006	0.2991		0.0794
10.0		0.0005	0.9959	0.0036	0.0002	0.6494	0.3504		0.1000
10.1		0.0004	0.9951	0.0045	0.0001	0.5955	0.4044		0.1230
10.2		0.0003	0.9940	0.0057	0.0001	0.5390	0.4609		0.1585
10.3		0.0003	0.9926	0.0071	0.0001	0.4816	0.5183		0.1995
10.4		0.0002	0.9908	0.0090	0.0000	0.4246	0.5754		0.2512
10.5		0.0002	0.9886	0.0112		0.3696	0.6304		0.3162
10.6		0.0001	0.9858	0.0141		0.3177	0.6823		0.3981
10.7		0.0001	0.9822	0.0177		0.2700	0.7300		0.5012
10.8		0.0001	0.9777	0.0222		0.2271	0.7729		0.6310
10.9		0.0001	0.9721	0.0278		0.1892	0.8108		0.7944
11.0		0.0000	0.9653	0.0347		0.1546	0.8454		1.000
11.1			0.9567	0.0433		0.1284	0.8716		1.230
11.2			0.9461	0.0539		0.1047	0.8953		1.585
11.3			0.9330	0.0670		0.0850	0.9150		1.995
11.4			0.9171	0.0829		0.0687	0.9313		2.512
11.5			0.8979	0.1021		0.0554	0.9446		3.162
11.6			0.8747	0.1253		0.0445	0.9555		3.981
11.7			0.8472	0.1528		0.0357	0.9643		5.012
11.8			0.8150	0.1850		0.0285	0.9715		6.310
11.9			0.7777	0.2223		0.0228	0.9772		7.944
12.0			0.7360	0.2640		0.0182	0.9818		10.00
12.1			0.6882	0.3118		0.0145	0.9855		12.30
12.2			0.6368	0.3632		0.0116	0.9884		15.85
12.3			0.5821	0.4179		0.0092	0.9908		19.95
12.4			0.5252	0.4748		0.0073	0.9927		25.12
12.5			0.4679	0.5321		0.0058	0.9942		31.62
12.6			0.4111	0.5889		0.0046	0.9954		39.81
12.7			0.3568	0.6432		0.0037	0.9963		50.12
12.8			0.3058	0.6942		0.0029	0.9971		63.10
12.9			0.2592	0.7408		0.0023	0.9977		79.44
13.0	0.0000	0.0000	0.2175	0.7825	0.0000	0.0018	0.9982	0.0000	100.00

(*a*) Because of the difficulty in preparing distilled water free from carbon dioxide, the total carbon dioxide contained in each sample was determined by evolution in Knorr's apparatus, absorption in ascarite, and weighing. The pH values were determined electrometrically, using the hydrogen electrode. Inserting the determined values we obtain:

Table IV—Results after Correction for Carbon Dioxide

Ion	Concentration of Ion in Solution					
	Sample 1		Sample 2		Sample 3	
	Millimols/liter	*Milliequiv./liter*	*Millimols/liter*	*Milliequiv./liter*	*Millimols/liter*	*Milliequiv./liter*
Na	29.000	29.000	15.000	15.000	1.900	1.900
K	0	0	1.000	1.000	0	0
SO_4	7.000	14.000	3.000	6.000	0.500	1.000
Cl	5.000	5.000	1.000	1.000	0.700	0.700
Total PO_4	0	...	1.000	...	0	...
Total CO_2	1.150	...	1.177	...	0.441	...
pH	11.95	...	11.75	...	6.3	...

To illustrate the method, ions of carbonic and phosphoric acids in sample 2 are calculated below.

(*b*) Assuming the activity coefficient (α) equals 1, for an initial approximation, we obtain from Figure 1, when pH is 11.75:

	Millimols/liter	*Milliequiv./liter*	
$0.97 \times 1.177 =$	1.142	2.284	CO_3
$0.03 \times 1.177 =$	0.035	0.035	HCO_3
$0.17 \times 1.000 =$	0.170	0.510	PO_4
$0.83 \times 1.000 =$	0.830	1.660	HPO_4

(*c*) Then subtracting the sum of the milliequivalents per liter of sulfate, chloride, carbonate, bicarbonate, phosphate, and monohydrogen phosphate from the sum of the milliequivalents per liter of sodium and potassium, we obtain 4.511 milliequivalents per liter or 4.511 millimols per liter of hydroxyl ion.

(*d*) Using the values from sample 2 of Table IV and paragraph (*b*) to calculate Σcv^2 and reading the corresponding activity coefficients from Figure 2,

Ions	*Millimols/liter*	*Mols/liter*	v^2	cv^2	α
Monovalent	21.546	0.021546	1	0.021546	0.87
Bivalent	4.972	0 004972	4	0.019888	0.57
Trivalent	0.170	0.000170	9	0.001530	0.28
			$\Sigma cv^2 =$	0.042964	

(*e*) From Table I at pH of 11.75,

$$a_{OH^-}\cdot 10^3 = 5.661$$

$$\frac{a_{OH^-}\cdot 10^3}{\alpha} = \frac{5.661}{0.87} = 6.507 \text{ millimols OH/liter}$$

$$\frac{a_{CO_3^{--}}}{a_C} = 0.9679, \quad \frac{a_{HCO_3^-}}{a_C} = 0.0321$$

$$\text{Then } CO_3 = 1.177 \times \frac{0.9679/0.57}{0.9679/0.57 + 0.0321/0.87} = 1.152 \text{ millimols/liter}$$

$$\text{and } HCO_3 = 1.177 - 1.152 = 0.025 \text{ millimol/liter}$$

$$\frac{a_{HPO_4^{--}}}{a_P} = 0.8633, \quad \frac{a_{PO_4^{---}}}{a_P} = 0.1367$$

$$\text{Then } HPO_4 = 1.000 \times \frac{0.8633/0.57}{0.8633/0.57 + 0.1367/0.28} = 0.756 \text{ millimol/liter}$$

$$\text{and } PO_4 = 1.000 - 0.756 = 0.244 \text{ millimol/liter}$$

(*f*) Recalculating the hydroxyl ion as in paragraph (*c*) we obtain

OH by difference = 4.427 millimols/liter

a difference of 1.9 per cent from the value obtained in paragraph (*c*). The ion concentrations obtained in paragraph (*e*) may differ considerably from those obtained in paragraph (*b*). The calculation should then be repeated until two consecutive calculations agree within the limits desired (approximately 10 per cent).

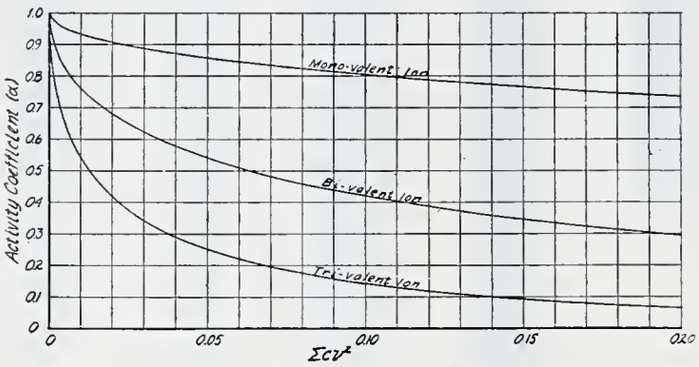


Figure 2—Ion-Activity Coefficient from Hückel and Debye Equation
Log $\alpha = -0.298\, \nu^2 \sqrt{\Sigma c \nu^2}$

Ion Valence	$\Sigma c\nu^2$ 1	2	3
α			
1.00	0	0	0
0.99	0.000214	0.000013	0.0000027
0.98	0.000866	0.000054	0.0000107
0.97	0.00197	0.000123	0.0000243
0.96	0.00354	0.000221	0.0000437
0.95	0.00559	0.000349	0.0000689
0.94	0.00812	0.000508	0.000100
0.93	0.0112	0.000700	0.000138
0.92	0.0148	0.000924	0.000183
0.91	0.0189	0.00118	0.000233
0.90	0.0236	0.00147	0.000291
0.85		0.00351	0.000693
0.80		0.00661	0.00131
0.75			0.00217
0.70			0.00334
0.65			0.00487
0.60			0.00684

(*g*) Converting the values obtained in paragraph (*d*) and paragraph (*e*) to parts per million by means of the factors given in Table I:

Millimols		*Valence*		f_2		*P. p. m.*
1.152	×	2	×	30.0	=	69.1 CO_3
0.025	×	1	×	61.01	=	1.5 HCO_3
0.244	×	3	×	31.68	=	23.2 PO_4
0.756	×	2	×	48.02	=	72.6 HPO_4
6.507	×	1	×	17.008	=	110.6 OH (calcd. from pH value)
4.427	×	1	×	17.008	=	75.3 OH (calcd. by difference)

The activities of the various ions may be calculated by multiplying the ion concentration by the activity coefficient, α, as obtained in paragraph (*d*). The activities so obtained (not the concentrations) should be used in solubility calculations to determine the character of precipitate or scale that would deposit from the water.

A summary of the results for the three samples and a comparison with various standard methods is given in Table V.

The total carbon dioxide (regardless of its form of combination) may be calculated from the titrations with fair accuracy if the pH at the end points is determined. For example, 25 ml. of sample 1 were titrated with 0.02 *N* sulfuric acid and electrometric pH run at the phenolphthalein and methyl orange end points. The calculations were as follows:

	pH	Ml. 0.02 *N* H_2SO_4
Methyl orange	4.6	24.82
Phenolphthalein	7.05	23.58
		1.24

$1.24 \times \frac{1000}{25} \times \frac{1}{50} = 0.992$ millimol/liter H^+ to change from pH 7.05 to pH 4.6

From Table I, if we assume that activity coefficients are equal, and

Let C = millimols of CO_2/liter;

	Millimols/liter	C
At pH 7.05	H_2CO_3	= 0.2036
	HCO_3	= 0.7960
	CO_3	= 0.0004
And at pH 4.6	H_2CO_3	= 0.9863
	HCO_3	= 0.0137
	H	= 0.0251

Ion	Quantity	Requires (*Millimols* H^+)	Forms	
CO_3	0.0004 C	0.0004 C	0.0004 C	HCO_3
HCO_3	(0.7960 + 0.0004 − 0.0137) C	0.7827 C	0.7827	H_2CO_3
		0.7831 C		

Millimol/liter H^+ = 0.992 = 0.7831 C + 0.0251, to change pH from 7.05 to 4.6, from which C = 1.234 millimols/liter

This compares quite well with the value 1.15 determined by evolution and weighing the carbon dioxide.

Inspection of Table I shows that best results from the titrations will be obtained if pH values of 8.5 and 5.0 are taken as data, under which conditions the formula becomes

$$H^+ = 0.0132 + 0.974\,C + 0.966\,P$$

where H^+, C, and P are millimols of H^+ ion required to change the pH of one liter of water containing C millimols of carbonate compounds and P millimols of orthophosphate compounds from pH of 8.5 to pH of 5.0. If P is known, C may be calculated from this formula and the results used in conjunction with the original pH of the water, in the same manner as the example (sample 2) calculated above. In case the water is not completely analyzed, $\Sigma c\nu^2$ cannot be calculated and we must assume that the ion concentrations equal their activities.

Table V—Summary of Results for Three Samples

Determination	A.P.H.A.(*1*)	Winkler(*6*)	Excess Acid(*2*)	Equilibrium Data
		Sample 1: pH, 11.95		
HCO_3	0	0	0	1.2
CO_3	107.6	99.0	46.1	67.8
OH by method	290.2	293.5	307.6	184.5
OH by difference	...	...	...	131.3
		Sample 2[a]: pH, 11.75		
HCO_3	0	0	0	1.5
CO_3	158.6	154.7	30.7	69.1
HPO_4	...	...	...	72.6
PO_4	...	...	...	23.2
OH by method	182.8	184.6	219.1	110.6
OH by difference	...	...	...	75.3
		Sample 3: pH, 6.3		
Free CO_2	4.0	...	4.0	11.2
HCO_3 by method	26.0	...	20 8	11.4
HCO_3 by difference	...	...	...	12.2

[a] Alkalinities by first three methods were not corrected for phosphate.

Conclusions

(1) Ion concentrations derived by this method are in agreement with physico-chemical theory.

(2) The method may be applied to any weak acid whose dissociation constant is known.

(3) The application of the method leads to a practical and theoretically correct solution of the problem of corrosion inhibition and scale prevention in industrial waters.

(4) It must be remembered that the calculations have been made from data determined at 25° C. and do not apply at higher temperatures. This points to the need for the following data so that the problems of corrosion and scale formation at higher temperatures may be logically attacked:

(*a*) Accurate dissociation constants for the weak acids and water throughout the temperature range in which water is used.
(*b*) Means for determining or calculating pH values at high temperatures.
(*c*) Determination of the activity coefficient of the ions involved at high temperatures or modification of the Debye and Hückel equation for use at these temperatures.

Acknowledgment

The author is indebted to J. C. Warner and H. Seltz, Carnegie Institute of Technology, for their coöperation in the derivation of the formulas, and to the laboratory staff of the Duquesne Light Company for their assistance in making the analyses.

Literature Cited

(1) American Public Health Assocn., "Standard Methods of Water Analysis," 6th Ed., p. 32 (1925).
(2) Hall et al., Carnegie Inst. Tech., *Bull.* **24**, 162 (1911).
(3) Lewis and Randall, "Thermodynamics," p. 311, McGraw-Hill, 1923.
(4) Lewis and Randall, *Ibid.*, p. 327.
(5) Noyes, *J. Am. Chem. Soc.*, **46**, 1099 (1924).
(6) Treadwell and Hall, "Analytical Chemistry," Vol. 2, p. 485, Wiley, 1927.

Simple Laboratory Autoclave[1]

Harold A. Cassar[2]

Technical Service Division, Standard Oil Company of New Jersey, Elizabeth, N. J.

THE difficulty of obtaining small autoclaves (200 to 500 cc.) and the expense of the larger ones induced the author to design the simple type described below. The cost of this type was in the neighborhood of twenty dollars.

Description of Autoclave

The autoclave consists of four main parts: bolt, outer head, inner head, and shell; and the following fittings: 2 short high-pressure nipples, one high-pressure tee piece, one pressure gage, and one needle valve. The construction is readily understood from Figure 1. The shell is made from mild steel tubing which is available in all diameters and thicknesses at large hardware stores. The bottom is closed by means of a well-fitting plug of the same material, which is then welded. The gasket for the inner head is made by pouring molten lead into the recess provided for it for low-temperature work, or by hammering a well-fitted disk of copper into the recess for temperatures above 180° C. No trouble was ever experienced in making the joint tight, and one of the advantages of this type of head is that it can be closed down in a few seconds, a very important consideration when one is dealing with liquefied gases such as ammonia or propylene, which can be put in the autoclave in the liquid state in large test tubes only so long as the operation of closing the autoclave is rapid.

The operation of closing the autoclave consists of pressing the inner head down firmly onto the lips of the shell, screwing the outer head loosely onto the shell, and tightening the bolt by applying one wrench to the hexagon cut on the top of the outer head, and the other wrench to the square head of the bolt. As an added convenience, the bolt can be cut in the form of a differential screw, the left-handed portion of the thread screwing into a knob left on top of the inner head, a device which enables one to use much smaller wrenches, but naturally raises the expense of producing the article.

Use of Autoclave

The charge is best put into a large test tube which fits snugly into the shell of the autoclave. The reactions usually carried out in sealed glass tubes can be run very advantageously in the smaller sizes of autoclaves. The pressure gage enables one to follow the course of the reaction. The valve is opened at the end of the experiment so that there is no danger in opening the autoclave, an operation which has caused many unpleasant accidents when using glass tubes. Time is saved both in closing and in opening the autoclave, and the difficulty of sealing glass tubes containing volatile liquids, or worse still, chemicals that attack the glass when hot and ruin the seal by frosting the glass, or that evolve poisonous vapors when heated, is entirely done away with.

On removing the outer head after an experiment, the inner head will usually be found to stick to the lips of the shell. However, it is easily pried loose with a screw driver applied between the lower edge of the inner head and the ledge on top of the shell. It is for this operation that the lips of the shell have been made higher than was otherwise necessary.

The autoclave is best heated in a steam oven for low temperatures, or in an oil bath with simple thermostat for higher temperatures. A safety valve is not included, since it is

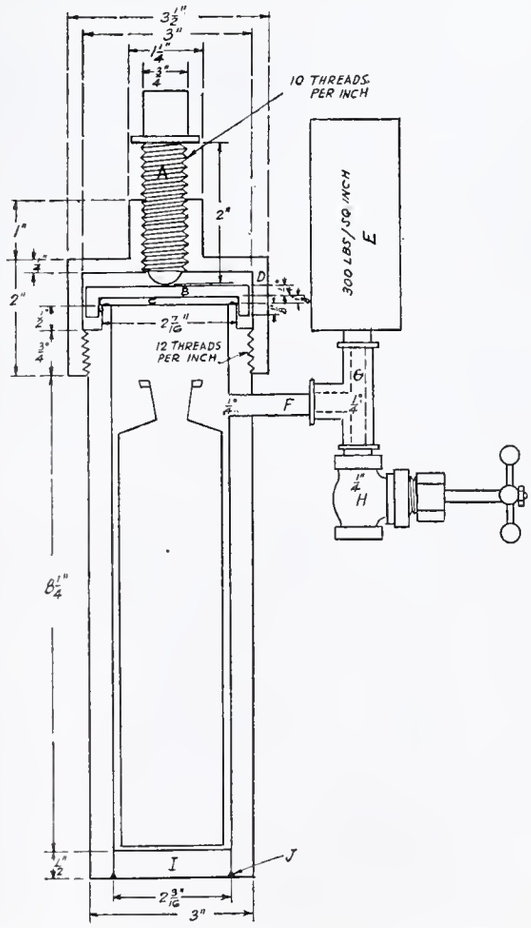


Figure 1—Simple Autoclave for Research Use

A—Bolt
B—Inner head
C—Copper or lead gasket
D—Outer head
E—Pressure gage
F—High-pressure nipple
G—High-pressure tee piece
H—Needle valve
I—Shell
J—Weld

[1] Received February 4, 1931.

[2] Present address, the Massachusetts Institute of Technology, Cambridge, Mass.

unreliable in small sizes and gives one a false sense of security. By running preliminary experiments in small autoclaves that can be readily dropped into a pail of water should the pressure become too high, and by avoiding the use of straight oxygen or of acetylene under combined pressure and temperature, accidents should not occur.

Microanalysis with an Ordinary Balance

I—Determination of Nitrogen by Micro-Dumas Method[1]

Wm. J. Saschek[2]

Laboratory of Microchemistry, Washington Square College, New York University, New York, N. Y.

MANY laboratories engaged in industrial analysis or research find it necessary or convenient to carry out numerous quantitative nitrogen determinations. The macro-Dumas method is tedious and time-consuming. The many advantages of the micro methods of elementary analysis devised by Pregl are so apparent that quite a number of adaptations have been made to utilize these methods in ordinary industrial work. An obstacle to a general adoption of the micro methods has been the cost and elaborate operating conditions of the micro balance required (*2, 3, 6, 7*). The usual method of attacking this problem is to increase the weight of the sample from the 2 to 5 mg. used by Pregl to 20 to 30 mg., and use an analytical balance of very high sensitivity such as 0.05 mg. (*4, 8*). These methods, however, do not retain all the advantages of Pregl's micro methods. In the first place, a balance of such high sensitivity costs almost as much as a micro balance. Second, the time of analysis, on account of the larger sample, is not very much shorter than the ordinary macro method. Furthermore, the apparatus used is considerably more complicated than that employed by Pregl.

One method retaining Pregl's apparatus in its entirety, but still avoiding the use of a microbalance, was worked out in this laboratory (*5*). Briefly, this method consists in dissolving the sample in a suitable solvent, spreading an aliquot portion of this solution on copper oxide in the mixing tube, and evaporating the solvent. While this method gives fairly good results, it was believed that there was room for further improvement. In the first place, the choice of a suitable solvent presents some difficulty where the solubility of the unknown substance in various organic solvents is not known. Then, in transferring the aliquot portion from the bottle to the mixing tube, some solvent is lost both from the sample and from the solution in the bottle, thereby introducing an error. Difficulty may also be experienced in removing the solvent after weighing.

In order to overcome these difficulties, a solid mixture was employed in place of the solution. Since the sample must be thoroughly mixed with copper oxide before introducing into the combustion tube, fine precipitated copper oxide was used as the base of the mixture. A comparatively large sample (0.1 gram) was ground up with a large amount of copper oxide (5 grams), and after thorough mixing, an aliquot portion of about 0.2 gram was taken for analysis.

If uniform distribution of the substance in the copper oxide is assumed and the aliquot sample is weighed out to within 0.1 mg. it can be seen that the sample of the substance has been weighed to 0.001 mg., which is the accuracy of the microbalance. If the mixture is ground fine so that no particle is larger than 0.05 mm. in diameter, the error due to sampling can be calculated by the formula of Baule and Benedetti-Pichler (*1*):

$$M = \frac{P_1 - P_2}{\sqrt{E}} \sqrt{v.\delta.p_1(1 - p_1)}$$

where M = "absolute average deviation" from theoretical percentage of element
P_1 and P_2 = percentage of element to be determined (N_2) in two components of the mixture (organic nitrogenous substance and copper oxide)
E = weight of entire sample
v = volume of single particle
δ = density of mixture
p_1 = ratio of number of particles of substance to be analyzed to total number of particles in mixture

To illustrate: If we take a substance containing 50 per cent nitrogen and mix it with fifty times as much copper oxide, the mixture should have practically the same specific gravity as pure copper oxide, since the small amount of organic substance will not affect it to an appreciable extent. If ground in an agate mortar, the particles will have a maximum diameter of 0.05 mm. Substituting in the formula we have

$$M = \frac{50 - 0}{\sqrt{200}} \sqrt{125.10^{-6}.6.0.02.(1 - 0.02)} = 0.01\%$$

Thus it can be seen that using a substance containing 50 per cent nitrogen, the absolute average deviation from the correct percentage due to sampling is 0.01 per cent; in other words, the per cent nitrogen obtained for the above substance will not be over 50.01 per cent nor under 49.99 per cent. These calculations are based upon the most unfavorable conditions. In actual practice the particles are much smaller, and the nitrogen content very rarely is as high as 50 per cent.

Table I—Results of Analyses of Samples
(Substance used, 0.1000 gram)

Substance	CuO	Mixture Weighed Out	Content of Substance	Nitrogen Obtained Volume	Temp.	Pressure	
	Grams	*Gram*	*Mg.*	*Cc.*	*° C.*	*Mm.*	*%*
o-Toluamide	4.9000	0.3285	6.570	0.586	22	762	10.35
		0.3168	6.336	0.550	17	769	10.34
		0.3306	6.612	0.581	20	769	10.36
		0.3034	0.068	0.544	24	756	10.25
		0.3318	6.636	0.502	22	764	10.37
						Av.	10.33
						Theory	10.36
Acetanilide	4.9000	0.2528	5.056	0.458	20.5	761	10.55
		0.2288	4.576	0.409	27	768	10.27
		0.2802	5.604	0.501	27	768	10.28
		0.2506	5.012	0.446	25	765	10.26
						Av.	10.34
						Theory	10.37
Acetanilide	4.9000	0.2643	5.286	0.481	26	761	10.40
		0.2630	5.260	0.484	29	767	10.49
						Av.	10.44
						Theory	10.37
Azobenzene	5.0000	0.2256	4.424	0.580	20	767	15.41
		0.1402	2.749	0.360	22	773	15.41
		0.1716	3.365	0.444	21	767	15.46
						Av.	15.43
						Theory	15.39
Benzamide	5.0000	0.1914	3.752	0.364	23	767	11.30
		0.3102	6.082	0.582	21	773	11.30
						Av.	11.30
						Theory	11.56

[1] Received February 13, 1931.

[2] Present address, Department of Biological Chemistry, College of Physicians and Surgeons, Columbia University, New York, N. Y.

A mixture containing about 2 per cent of the substance to be analyzed was found to be suitable. It was prepared as follows: 0.1000 gram of the finely powdered substance was first thoroughly mixed on high-gloss paper with 4.9000 grams of pulverized copper oxide which had been previously ignited and ground in the mortar. It is not necessary to have the sample and copper oxide in exactly this proportion; it was only used to simplify final calculations. The mixture was then transferred quantitatively to a glass or, preferably, an agate mortar, where it was ground for several minutes. The particles of this mixture had a maximum diameter of 0.02 mm. which is much less than that assumed in the theoretical discussion. Aliquot samples of about 0.2 gram were taken for analysis. The course of the analysis from this point on was the same as described by Pregl. The results are given in Table I.

To sum up, the economy and simplicity of Pregl's micro-Dumas determination of nitrogen have been retained in a method which eliminates the use of a microbalance when 0.1 gram of substance is available. It has the further advantage that as many analyses as desired can be made and the unused sample recovered by the use of a suitable solvent. If a more sensitive balance is available, or if so great an accuracy is not necessary, the amount of substance can be reduced still further.

Literature Cited

(1) Baule and Benedetti-Pichler, *Z. anal. Chem.*, **74**, 442 (1928).
(2) Emich, "Lehrbuch der Mikrochemie," Muenchen, 1926.
(3) Flaschentraeger, *Z. angew. Chem.*, **39**, 717 (1926).
(4) Lauer and Sunde, *Mikrochemie*, Pregl-Festschrift, 235 (1929).
(5) Niederl, Trautz, and Saschek, *Ibid.*, Emich-Festschrift, 219 (1930).
(6) Pregl, "Die Quantitative organische Mikroanalyse," Springer, 1930. Translated by Ernest Fyleman, Blakiston, 1930.
(7) Schwarz-Bergkampf, *Z. anal. Chem.*, **69**, 321 (1926).
(8) Wise, *J. Am. Chem. Soc.*, **39**, 2055 (1917).

The Hehner Test for Formaldehyde[1]

Charles C. Fulton

U. S. Industrial Alcohol Bureau, Omaha, Neb.

The Hehner test can be improved by using bromine for the oxidizing agent and by diluting the sulfuric acid somewhat before adding the milk to be tested. The color can be developed in a zone, or uniformly throughout the solution. The improved test is sensitive to 1 part of formaldehyde in 1,000,000 of milk.

When a solution of formaldehyde in milk is underlaid with concentrated sulfuric acid containing a little ferric salt or other oxidizing agent, a violet color develops at the junction. This is the well-known Hehner test, introduced in 1895 and still in use. The reaction with formaldehyde depends on the tryptophan component of the proteins. Tryptophan is one of the amino acids. Proteins other than those of milk can be used for the test so long as they contain a moderately large proportion of tryptophan. Egg albumin is sometimes used. Peptone has been highly recommended for this test or for the Leach test, which substitutes concentrated hydrochloric acid and heating for the concentrated sulfuric acid. However, some samples or kinds of peptone give only a feeble reaction.

The test is an aldehyde-oxidation reaction of an aromatic amine, analogous to the aldehyde-oxidation reactions of phenols, which have been previously discussed (*2*). Experiments with formaldehyde and tryptophan itself show that bromine is the best oxidizing agent, and that the proper strength of sulfuric acid for the strongest color is secured by diluting the concentrated acid with from half its volume up to an equal volume of water. Tryptophan alone, in aqueous solution, gives a purplish pink color with bromine but this bromine test for tryptophan cannot be obtained in strong sulfuric acid solution and does not interfere at all with the formaldehyde reaction.

If the conditions found most suitable for the tryptophan reaction are applied to the detection of formaldehyde with milk, the test is considerably improved. The usual test, if carefully performed, is sensitive to about 1 part of formaldehyde in 300,000 of milk. On account of the color obtained with a blank (yellowish green changing to brown), and the charring produced if the concentrated sulfuric acid is accidentally partly mixed with the milk suddenly, the test is none too reliable for very small proportions of formaldehyde—that is, less than 1 part in 100,000. The A. O. A. C. description (*1*) sets the sensitivity of the Hehner test at about 1:10,000. This is an obvious error, as the test is easily more sensitive than the Rimini, or phenylhydrazine hydrochloride and sodium nitroprusside test, for which the sensitivity is set at 1:70,000 to 1:80,000. Leach sets the sensitivity of his test, which is similar to Hehner's, at 1:250,000 (*3*).

The improved test is sensitive to 1 part of formaldehyde in 1,000,000 of milk and it has certain other advantages also. Two methods of making the test are given in the following paragraphs. The first gives a zone reaction, as in the ordinary Hehner test, and the second gives a uniform color throughout the solution.

First Method—Dilute 5 cc. of concentrated sulfuric acid with 1 cc. of water, cool, and put 3 cc. of this diluted acid in a test tube. Drop in a small crystal of potassium bromide. Shake, then overlay at once with 1 cc., or a little more, of the milk to be tested, without mixing. Bromine, set free by the action of the strong acid, effects the oxidation. If formaldehyde is present, even as little as 1 part in 1,000,000 parts of milk, a violent zone quickly develops. If no violet appears by the time the acid has become orange-yellow, the test is negative. Owing to the prior dilution of the acid, the color forms in a fairly broad zone rather than in a narrow ring. The escape of bromine and hydrobromic acid also tends to mix the two solutions. The reaction is strongest with about 1 part formaldehyde in 50,000 of milk. The color then spreads through practically the whole of the liquid in the test tube, and is strong violet at the bottom, ranging to deep red at the center, and back to purple at the top. For good results the formaldehyde should not exceed about 1 part in 1000; this is true of the usual Hehner test also

Second Method—Dilute 8 cc. of concentrated sulfuric acid with 5 cc. of water, cool, and put 4 cc. of this diluted acid in a test tube. Add 1 cc. of the milk to be tested, and mix with running water while cooling. A clear and practically colorless solution should result, unless a large proportion of formaldehyde is present (see Table I). The curd at first formed is redissolved. Prepare a bromine oxidizing solution by mixing equal volumes of concentrated sulfuric acid and saturated bromine water, and cooling. Add about 0.5 cc. of the oxidizing solution to the sulfuric acid–milk solution, and shake. In the presence of formaldehyde a violet color develops at once, a color ranging to light purplish pink for very small proportions of formaldehyde. The blank is

[1] Received January 21, 1931.

practically colorless, but has a faint pink tinge. The color with as little as 1 part in 1,000,000 of formaldehyde is easily distinguishable. Table I gives the results with various proportions of formaldehyde.

The above proportions of acid, water, and milk can be varied a little. Two cubic centimeters of concentrated sulfuric acid can be diluted with 1 cc. of water, and this diluted acid mixed with 1 cc. of the milk to be tested. These proportions will give a stronger purple with very little formaldehyde (1 part in 500,000 or less), but on the other hand the blank then shows a distinct though slight pink color.

The faint pinkish color obtained in the blank in this method is probably due to a trace of formaldehyde formed from the carbohydrate of the milk by the action of the strong acid.

The second method is particularly well suited to the detection of formaldehyde in a distillate. Instead of diluting the concentrated sulfuric acid with pure water, dilute it with the distillate to be tested, and then mix with pure milk.

All varieties of the Hehner test are spoiled by a large proportion of formaldehyde. This is not a defect of the Hehner test alone, for a number of other formaldehyde tests have the same flaw. However, when enough formaldehyde is present to interfere seriously with the test, its odor can be distinguished.

Table I—Reactions with Bromine Oxidation and Formaldehyde in Hehner Test

Formaldehyde in Milk	Before Adding Bromine Soln.	After Adding Bromine Soln.
Parts		
None	None	Whitish, faint pink tinge
1 in 1,000,000	None	Slight purple-pink
1 in 500,000	None	Light pink-purple
1 in 100,000	None	Deep violet
1 in 50,000	None	Strong deep violet
1 in 10,000	Light greenish yellow	Intense violet
1 in 1000	Greenish yellow, some undissolved material	Becomes purplish pink, undissolved matter brownish
1 in 100	Yellowish white, undissolved material	Becomes somewhat brownish; test negative

Literature Cited

(1) Assocn. Official Agr. Chem., Methods, p. 132 (1925).
(2) Fulton, *J. Assocn.-Official Agr. Chem.*, **12**, 434 (1929).
(3) Leach and Winton, "Food Inspection and Analysis," p. 165, Wiley, 1920.

The Opium Alkaloids as Reagents for Formaldehyde[1]

Charles C. Fulton

U. S. Industrial Alcohol Bureau, Omaha, Neb.

Phenolic compounds (phenols and ethers of phenols) in general, and certain of the opium alkaloids in particular, are useful as reagents for formaldehyde. The tests are best made by mixing some of the aqueous solution to be tested (preferably a distillate) with concentrated sulfuric acid in appropriate proportion, and applying this solution to the alkaloid. An oxidizing agent is also added for the more sensitive tests. Morphine and apomorphine give good phenol-aldehyde tests. These tests are sensitive to about 1 part formaldehyde in 5000 to 6000 parts of water. With the addition of the oxidizing agent apomorphine, codeine, pseudomorphine, and papaverine give the best tests. These reactions are not specific for formaldehyde, as other aldehydes may give similar colors, but under the conditions and with the precautions given they provide fairly certain identification, as well as detection of very small quantities. They are sensitive to as little as 1 part formaldehyde in 500,000 or even 1,000,000 parts of aqueous solution.

The opium alkaloids, particularly morphine and apomorphine, have had considerable use in detecting formaldehyde. The reaction is that of a phenol with an aldehyde in the presence of strong acid, producing a color.

Tests much more sensitive both to the phenolic compound and to the aldehyde can be obtained by the addition of an appropriate oxidizing agent to the mixture (*4*). The alkaloids most suitable for such tests are apomorphine, codeine, pseudomorphine, and papaverine. (Phenolic tests in strong acid succeed with ethers of phenols as well as with true phenols.) The tests with the addition of an oxidizing agent can be so made as to be sensitive to 1 part of formaldehyde in 1,000,000 parts of aqueous solution.

Phenol-Aldehyde Reactions

Morphine—The test with morphine is usually made by dissolving the alkaloid in concentrated sulfuric acid and adding a drop or two of the solution to be tested. It is better to dilute the sulfuric acid with the aqueous formaldehyde solution and then apply the mixture to the morphine, but the texts do not state what proportion of acid and aqueous solution should be used for such a test. There is a too-prevalent assumption that phenol-aldehyde reactions take place best in full-strength, concentrated sulfuric acid, but this assumption is often erroneous. The morphine reaction is best in sulfuric acid of 75 to 85 per cent sulfuric acid. With full-strength sulfuric acid, the reaction is not very sensitive to formaldehyde, and the color with small amounts of the aldehyde is not the brilliant crimson to purple obtained with more formaldehyde or more dilute acid, but is a dark blue that develops gradually. Hence the test made by dissolving morphine in concentrated sulfuric acid on a watch glass, and floating this on the liquid to be examined (*1*, *3*) by way of exposing the acid solution to the vapor of formaldehyde, is not a good one. It is better to prove that the reaction is due to a volatile substance by using a distillate from the suspected solution. Mix 1 cc. of the distillate with 2 to 5 cc. of concentrated sulfuric acid, while cooling; then apply to morphine on a spot plate. A purple-red to purple color denotes formaldehyde. The color appears practically at once down to about 1 part of formaldehyde in 6000 of water. The test can be carried out as a zone reaction if desired.

Apomorphine—The above remarks in regard to morphine apply in large part to apomorphine also. With the latter, the color in concentrated acid is purple, rapidly darkening to blue-black and then changing to dark green; with only a little formaldehyde the color develops as dark green. With acid of 75 to 85 per cent sulfuric acid, the purple to violet color is better and more persistent. Gettler recommended apomorphine over morphine. He mixed 5 cc. concentrated sulfuric acid with 2 cc. of distillate from the suspected solution, then added the alkaloid (*5*). "Allen's" misrepresents him as recommending apomorphine for Bonnet's test (*3*).

[1] Received January 21, 1931.

The simple phenol-aldehyde reaction is probably as well obtained with morphine as with apomorphine, but with the addition of an oxidizing agent, even in the merest trace, apomorphine gives a far more sensitive test. This phenomenon is often noticed when no oxidizing agent is intentionally added. In fact, it probably takes place to a slight extent under the action of the air. Moreover, the color developed is similar to that of the simple phenol-aldehyde reaction. This probably accounts for the recommendation of a number of different investigators that apomorphine rather than morphine be used in the phenol-aldehyde test for formaldehyde.

Phenol-Aldehyde-Oxidant Reactions

The tests with the addition of an oxidizing agent are carried out as follows:

Mix concentrated sulfuric acid, while cooling, with some of the suspected solution, or better with a distillate from the suspected solution, in a proportion suitable to the alkaloid used for the test. Also mix one of the two oxidizing solutions given below with concentrated sulfuric acid in the same proportion. Then add about 0.4 cc. of the acid solution believed to contain the aldehyde to a little of the alkaloid on the spot plate, and stir with a glass rod. The color of the simple phenol-aldehyde reaction will be noticed at this point with apomorphine or codeine, if the formaldehyde exceeds about 1 part in 5000 of aqueous solution. Next add a single drop of the sulfuric acid solution of the oxidizing agent and stir it in. The color of the phenol-aldehyde-oxidant reaction then develops. The test is unmistakably sensitive to 1 part formaldehyde in 500,000 of water with apomorphine, codeine, or pseudomorphine, and to 1 part in 100,000 with papaverine. The results are given in Tables I, II, and III.

Table I—Color Reactions of Apomorphine in Test for Formaldehyde
2 cc. concd. H_2SO_4 with 1 cc. aqueous formaldehyde soln.
Ferric oxidizing agent

Formaldehyde in Aqueous Soln.	Before Adding Oxidizing Agent	After Adding Oxidizing Agent
Parts		
None	None	Light salmon
1 in 1,000,000	None, or a very slight pink	Weak (dull) pink
1 in 500,000	None, or a very slight pink	Quickly purplish pink
1 in 100,000	None, or a very slight pink	Good purplish pink; gradually purplish red
1 in 50,000	None, or a very slight pink	Purplish pink, soon purplish red
1 in 10,000	Faint yellowish; purplish if allowed to stand	Purple changing to strong deep purple-red
1 in 1000	Slight yellowish changing to light purple	Strong violet, changing to strong purple, changing to strong red-purple, then to deep purple-red; gradually dark red
1 in 100	Light violet rapidly darkening	Deep blue, changing to strong violet at once; to strong red-purple soon; gradually dark red

Table II—Color Reactions of Codeine in Test for Formaldehyde

Formaldehyde in Aqueous Soln.	3 cc. Concd. H_2SO_4 with 1 cc. Aqueous Formaldehyde Soln. Ferric Oxidizing Agent		2 cc. Concd. H_2SO_4 with 1 cc. Aqueous Formaldehyde Soln.
	Before adding oxidizing agent	After adding oxidizing agent	After adding nitric acid oxidizing agent
Parts			
None	None	None	Light yellow
1 in 1,000,000	None	Slight blue, become light blue	Light blue-green, changing to light green; gradually green-yellow
1 in 500,000	None	Slight blue quickly becomes light blue	Quickly light blue, changing gradually to weak dull green
1 in 100,000	None	Good blue	Deep blue
1 in 50,000	None	Good blue	Strong deep blue
1 in 10,000	Practically none	Blue	Strong deep blue
1 in 1000	Soon purple	Color changed to lighter blue-green; gray-blue, then dark blue; gradually dark brown	Light gray, changing to weak gray-green, then to dull gray-blue
1 in 100	Purple	Color changed to light green, light brownish gray, then violet-gray; gradually blue-black; gradually dark brown	Color changed to light gray, then to brown

Table III—Color Reactions of Psuedomorphine and Papaverine in Test for Formaldehyde after Adding Oxidizing Solution

Formaldehyde in Aqueous Soln.	Pseudomorphine	Papaverine
	2 cc. concd. H_2SO_4 with 1 cc. aqueous formaldehyde soln. Ferric oxidizing agent	4 cc. concd. H_2SO_4 with 1 cc. aqueous formaldehyde soln. Nitric acid oxidizing agent
Parts		
None	Slight yellowish	Greenish yellow, fading to slight yellowish
1 in 1,000,000	Light green, slightly bluish	Greenish yellow, fading to slight yellowish
1 in 500,000	Light blue-green	Light green, gradually fading to yellowish
1 in 100,000	Greenish blue, soon becoming good blue-green	Blue, gradually fading somewhat
1 in 50,000	Blue, slightly greenish changing to deep blue-green	Blue
1 in 10,000	Blue, very slightly greenish; changing to deep blue-green	Intense deep blue
1 in 1000	Blue, very slightly greenish; changing to deep blue-green	Intense deep blue
1 in 100	Blue, changing to deep blue-green	Intense deep blue

The two oxidizing solutions are as follows: ferric, a 10 per cent solution of ferric sulfate in water; nitric acid, 5 drops of concentrated nitric acid in 50 cc. water. These solutions are mixed with concentrated sulfuric acid in appropriate proportion before use.

The tests are not specific for formaldehyde, as other aldehydes may give similar colors. However, if they are performed as described, using a distillate from the suspected solution, and two or three different alkaloids, the identification is fairly certain.

Apomorphine and Codeine—Codeine has been previously recommended for a test of this kind, but apparently the reaction was not understood (*2*).

Both codeine and apomorphine give the simple phenol-aldehyde reaction if the formaldehyde exceeds about 1 part in 5000 in the aqueous solution, and the test with the addition of the oxidizing agent is changed or even spoiled if this much formaldehyde is present. The color is best developed in acid as weak as can well be used, since the oxidizing agent by itself produces too much color in stronger acid.

Pseudomorphine and Papaverine—The more formaldehyde present, the better the reactions with these two alkaloids succeed. Neither gives the simple phenol-aldehyde reaction in diluted sulfuric acid. With pseudomorphine, however, so little oxidizing action is required that a slight green almost invariably develops when the formaldehyde exceeds 1 part in 10,000, even though no oxidizing agent is intentionally added. With papaverine no color appears until the addition of the oxidizing agent.

The pseudomorphine test gives the least proof that formaldehyde is present, as most aldehydes give either a blue or a green color with it, under appropriate conditions. The ferric oxidizing agent by itself gives a dull green color with pseudomorphine in concentrated acid, but not in the weakened acid used for the aldehyde test.

Papaverine requires stronger acid and a stronger oxidizing action than is necessary with the other alkaloids, and the test is somewhat less sensitive. On the other hand, it gives the most nearly specific test for formaldehyde. Probably there are very few other aldehydes combining readily enough with papaverine to give the blue color under the conditions of this test.

Literature Cited

(1) "Allen's Commercial Organic Analysis," Vol. 1, p. 327, Blakiston, 1923.
(2) Aloy and Valdiguie, *J. pharm. chim.*, **4**, 390 (1926).
(3) Bonnet, *J. Am. Chem. Soc.*, **27**, 601 (1905).
(4) Fulton, *J. Assocn. Official Agr. Chem.*, **12**, 434 (1929).
(5) Gettler, *J. Biol. Chem.*, **42**, 311 (1920).

Generator for Production of Carbon Dioxide of High Purity[1]

Edgar J. Poth

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS, AUSTIN, TEXAS

FOR the production of a gas, such as carbon dioxide, it is often desirable that (1) its generation be effected entirely within glass containers devoid of rubber connections, (2) the apparatus be of such construction as to admit at the start of efficient removal of occluded gases, (3) the continuous or intermittent production of the gas in quantity and at any desired rate be assured without an excess escaping into the laboratory, and (4) the gas be of uniform and maximum purity.

Although the apparatus herein described has been employed in the Texas Laboratory solely for the generation of carbon dioxide in connection with the estimation of nitrogen by the combustion method, the principle of construction can be adapted to the production of many other gases. It is obvious that, where desired, the gas concerned can be delivered free of water vapor.

In general there are two methods employed in generating carbon dioxide: the action of an acid on a carbonate or bicarbonate, and the thermal decomposition of a bicarbonate. The first method is discussed by Böck and Beaucourt (*1*) at some length in a paper published in 1928. They cite several modifications to the routine of filling, as well as variations as to the form of Kipp generators, but finally conclude that the method of Pregel (*3*, *5*) is the preferable one. Furthermore, they conclude that the bicarbonate tube of von Brunner (*2*) can be made to yield a somewhat better grade of gas. But, owing to the fact that it must be swept free of air at each heating, the purity of the gas cannot be controlled as accurately as in the case of the Kipp.

Since that time the present author (*4*) has described a generator which enables one to store a quantity of carbon dioxide with complete assurance that it will represent a gas of a consistent high purity. After continuous use for a year this generator has fulfilled all claims advanced.

At times it is desirable to have an automatic or continuous generation of a gas. This feature is incorporated in the generator to be described. In its adaptation to the production of carbon dioxide, excellent results are obtained with the reactants 1:1 sulfuric acid and a saturated aqueous solution of acid potassium carbonate. The use of marble is inadvisable, because, in the author's experience, it is not possible to eliminate completely occluded air even after boiling out with water, treating with dilute acids, and pumping to a low pressure for several hours.

Construction and Operation of Generator

The accompanying figure is for the most part self-explanatory. A convenient design is with *A* and *B* made from 2- and 1-liter, round-bottomed, Pyrex flasks, respectively. *A* is charged with 500 grams of acid potassium carbonate dissolved in 1200 cc. of water, and *B* with 170 cc. of water followed by 170 cc. of concentrated sulfuric acid. The heat of dilution raises the temperature of the acid almost to the boiling point and thus contributes to the subsequent elimination of contained air. *D* and *E* are sealed, and the desired amount of water is introduced into the bubble counter, *G*. Then the T-shaped, three-way stopcock, *J*, with its perpendicular arm, *K*, filled with and extending into mercury, is temporarily connected through rubber tubing at *I*, and the entire system is evacuated with an oil pump simultaneously through *H* and *L*. The pumping is continued for about 15 minutes when the appropriate amount of mercury is run into *F*. Both during the pumping and for some time afterwards, the bicarbonate solution in *A* will evolve carbon dioxide. Besides being a great help in sweeping out the last traces of dissolved air from the solutions, this property is used in starting off the generator. After closing the T-shaped stopcock, it is disconnected from the suction pump at *L*. The evolution of carbon dioxide in *A* drives the gas into *B* to build up sufficient pressure to force acid into *A*

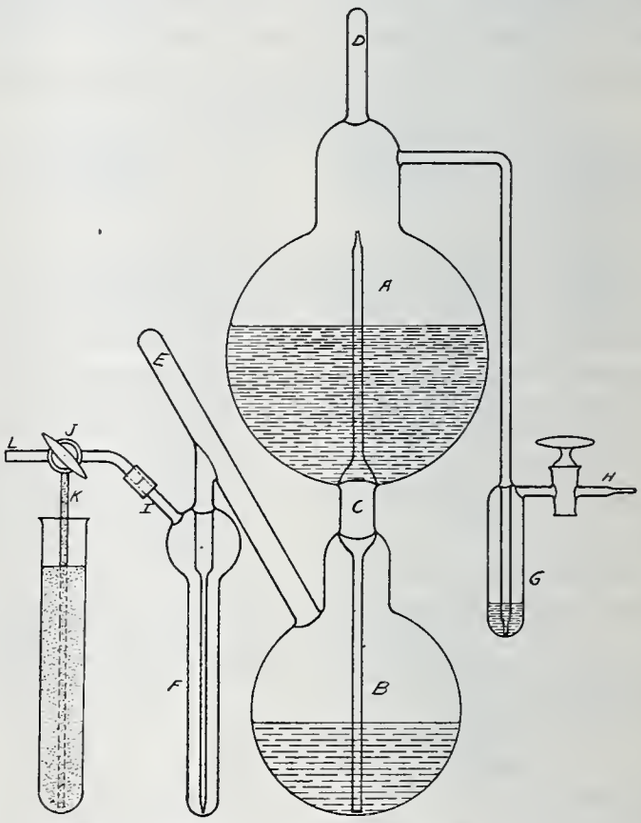


Figure 1—Generator for Production of Carbon Dioxide

upon evacuation through *H*. If *H* is closed immediately following the introduction of the acid, the gas generated will force more carbon dioxide into *B*. By repeating this procedure, sufficient pressure can be built up in *B* to force the mercury seal, *F*. During this process, the T-shaped stopcock is cautiously opened from time to time to ascertain when the pressure in *B* is equal to atmospheric pressure plus the height of the mercury column in *F*. When this is attained, the T-shaped stopcock can be removed, and the generator will deliver a stream of practically pure carbon dioxide whenever *H* is opened. As the apparatus cools, or after it has stood for long periods of time, it may be necessary to apply suction at *H* and again force acid into *A* to reëstablish the

[1] Received October 29, 1930. This paper is the outgrowth of an investigation of "The Nitrogen Compounds in Petroleum," listed as Project 20 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the coöperation of the Central Petroleum Committee of the National Research Council.

desired pressure in the system. Obviously, the basic principle of this generator can be adapted to the preparation of gases other than carbon dioxide.

This generator incorporates the following advantages: (1) it is compact and is constructed entirely of glass without ground-glass connections; (2) it can be warmed and pumped free of occluded gases; (3) it is sealed with mercury against contaminating atmospheric gases; (4) it has a novel automatic feeding arrangement; and (5) it utilizes its reactants completely without wasting any of the gas produced, even during long periods of standing.

Literature Cited

(1) Böck and Beaucourt, *Mikrochemie*, **6**, 79 (1928).
(2) Brunner, von, *Chem.-Ztg.*, **38**, 767 (1914).
(3) Hein, *Z. angew. Chem.*, **40**, 865 (1927).
(4) Poth, Ind. Eng. Chem., Anal. Ed., **2**, 250 (1930).
(5) Pregl, "Quantitative Organische Mikroanalyse," p. 98, Springer, 1930.

Improved Hydrogen-Electrode Cell for Determination of pH[1,2]

W. B. Bollen[3]

Idaho Agricultural Experiment Station, Moscow, Idaho

The cell described, constructed from usual laboratory materials, is widely applicable for rapid and accurate pH determinations. Novel features are (1) a Pyrex-Alundum porous-tip calomel electrode, (2) a salt bridge giving sharp, reproducible liquid junctions, and (3) a stirrer which centrifugally circulates through the sample a small constant volume of hydrogen under constant pressure. The stirrer-circulator especially adapts the hydrogen electrode to solutions containing dissolved carbon dioxide or other gases participating in H-ion equilibria. It also handles foaming liquids to advantage. Hydrogen saturation of the solution is effected in minimum time and true H-ion equilibrium is attained quickly. When side reactions interfere, voltage-time curves are useful in estimating the point of virtual H-ion equilibrium.

Typical data presented illustrate the rapidity, accuracy, and versatility of the apparatus.

The cell illustrated, developed after experience with numerous types of electrometric apparatus, satisfactorily meets the requirements for rapid and accurate pH determinations on a variety of solutions and suspensions. The hydrogen electrode, calomel electrode, and salt bridge are readily constructed from usual laboratory materials and give service with minimum attention.

A centrifugal circulator or stirrer which circulates a small constant volume of hydrogen through the liquid under constant pressure is a feature of the hydrogen electrode devised for use with liquids containing carbon dioxide or other gases participating in H-ion equilibria. It is especially applicable to pH determinations on solutions or suspensions of alkali soils containing carbonates. In such cases colorimetric methods as well as the quinhydrone electrode are often inapplicable, while the use of a bubbling-type hydrogen electrode results in removal of dissolved carbon dioxide with consequent shift in acid-base equilibria and increase in pH. Shaking electrode vessels of the type described by Clark (*3*) and Snyder (*6*) may be used, but their construction is beyond the skill of ordinary glass blowers and the mechanism for shaking is more complicated than that required for the stirrer. Since the stirrer effects hydrogen saturation of both solution and electrodes in minimum time, its general application is indicated.

By using the stirring electrode with a modification of the salt bridge designed by Waterman (*7*), the advantage of permanent contact, together with a sharp reproducible liquid junction permits readings at any time, whether the stirrer is in operation or not. It is thus possible to follow the voltage change during a determination from the beginning until a constant or maximum value is attained. This not only saves time but also permits a comprehensive voltage curve for guidance in determining the point of H-ion equilibrium.

[1] Received August 8, 1930.

[2] Published with approval of the director of the Idaho Agricultural Experiment Station as Scientific Paper 63.

[3] Now associate bacteriologist, Oregon Agricultural Experiment Station, Corvallis, Ore.

Construction of Hydrogen Electrode

The stirrer-circulator consists of a small glass T-tube fused to a glass rod or shaft of similar diameter. An axial opening, corresponding in size to the bore of the tubing, is provided in the T where it joins the shaft within the vessel. Another opening is provided in the center of the open-end cross tube at the bottom. A hard rubber bearing for the shaft is centered in a sulfur-free rubber stopper that has been carefully filed or ground on the lower two-thirds of the circumference to remove the taper and make a tight fit with the mouth of the vessel. Careful fitting of this stopper is essential; even a slight taper will result in its working loose when in contact with alkaline solution. The bearing should be accurately turned and drilled in a lathe, the upper half being drilled a few tenths of a millimeter oversize, so that the shaft fits with minimum play consistent with free operation. A shoulder for contact with the top surface of the stopper is provided for stability.

To hold the stirrer in place and to connect with the flexible shaft of a motor drive, a flexible coupling is made from a short piece of glass tubing fitted with a section of heavy-walled rubber tubing inside and projecting slightly beyond the upper end. The glass tube is of such inside diameter that it will rotate smoothly when slipped over the upper part of the hard rubber bearing; the rubber tube must fit snugly inside the glass tube and also hold firmly the driving end of the flexible shaft and the driven end of the stirrer shaft. Assembly is made by placing the coupling over the bearing and thrusting the stirrer shaft through the bearing and into the rubber tube inside the glass. To connect with the motor, the free end of the flexible shaft is brought into proper position and inserted in the upper end of the coupling.

The rubber stopper must be carefully bored to carry not only the stirrer bearing but also a hydrogen inlet tube and the hydrogen electrodes. Two of the latter are always used and connected to a double-throw switch so one may be checked against the other during every determination. If properly plated with either platinum or palladium black, both should come to equilibrium within a few seconds of each other and

agree within one millivolt. Whenever these conditions are not satisfied, both electrodes are removed, cleaned, and replated; this requires three to five minutes, far less time than will be lost by working with sluggish electrodes, and does away with a serious source of uncertainty.

Inasmuch as the hydrogen electrodes are of first importance in any hydrogen-electrode system, too much attention cannot be given to their preparation and care. The active surface is deposited according to directions given by Clark (*1*). Palladium is used in preference to platinum because of the

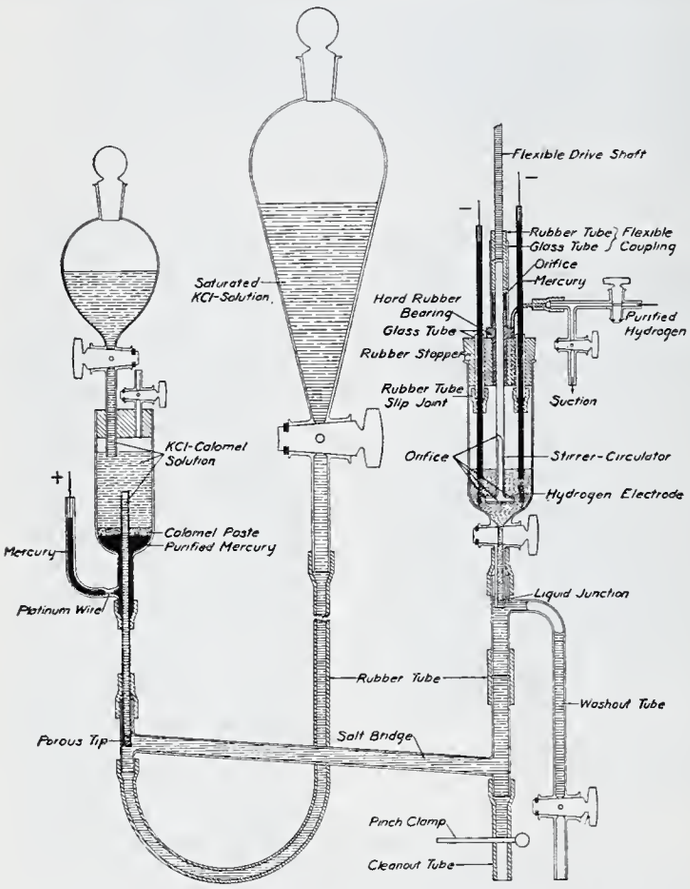


Figure 1—Hydrogen-Electrode Cell for pH Determination

ease with which unsatisfactory deposits may be removed by electrolysis in hydrochloric acid solution. Platinum and palladium-plated electrodes were simultaneously compared in a variety of solutions, and when deposits were made under comparable conditions, excellent agreement was found. When using current under a potential of four volts for making deposits from 3 per cent hydrochloric acid solutions containing 3 per cent of either metal, 12 to 15 seconds is the optimum time for plating the electrodes. A 10-second deposit tends to give low readings, while a 20-second deposit gives a sluggish electrode. A difference of even one second in the time of plating two electrodes that are used together is reflected by difference in the rates of attaining equilibrium. For this reason the practice of electrolyzing the electrodes simultaneously in the cleaning, plating, and charging solutions is generally followed. It is important that these solutions be carefully protected from contamination, and that the sulfuric acid solution used for charging the electrodes with hydrogen be freshly prepared for each day's run. As the plating solution becomes weaker, the time of deposition must be correspondingly increased, but after a 20-second optimum has been reached, it is advisable to increase the concentration.

To facilitate removal and replacement of the hydrogen electrodes, each of which consists of 3 or 4 cm. of No. 20 B & S gage platinum wire suitably spiraled and sealed into one end of a 15-cm. length of Pyrex tubing carrying mercury for electrical connection, two short lengths of larger glass tubing are inserted in the stopper and fitted with slip joints of rubber tubing at the lower end within the vessel. The size of these various tubes is so selected that the electrode tubes may be freely thrust through or withdrawn from below, the rubber forming tight joints.

It is desirable that all holes in the stopper be bored as nearly perpendicular to the face as possible to insure proper alignment of the electrodes with respect to the stirrer and walls of the vessel. The electrodes must be firmly held where the active surface will receive a copious wash of hydrogen bubbles and solution centrifugally thrown by the stirrer, but at the same time abrasion by contact with the vessel or stirrer must be avoided.

The electrode vessel is most conveniently made from an open-top separatory funnel of about 60 cc. capacity. The stem is cut to a length of 3 cm. and the bore in both plug and throat reamed out with Carborundum dust to a diameter of at least 3 mm. to provide ample conductivity. No grease is used on the stopcock. Aside from contributing to cleanliness, the absence of grease permits determinations to be made on electrolyte solutions denser than saturated potassium chloride. In such cases, with the stopcock necessarily closed, the moist ground glass gives the conductivity required.

Porous-Tip Calomel Electrode

The calomel electrode is provided with a porous tip for connection with the salt bridge. This tip also permits the half-cell to be used as a dipping electrode if desired. Parker and Dannerth (*4*) and Schollenberger (*5*) have described ground-glass plug tips, but these are difficult to construct. An equally effective and more serviceable tip can be easily prepared by sintering a 100-mesh mixture of equal parts of Pyrex glass and Alundum in one end of a Pyrex tube. A tube of appropriate size is sealed at one end and enough of the Pyrex-Alundum mixture introduced to give a column about 3 cm. long when well tamped down. This end is then placed in a blast flame and the mixture is gently tamped with a glass rod until incipient redness, to eliminate air bubbles. The rod is then withdrawn and heating continued until a temperature of approximately 950° C. has been maintained for 4 or 5 minutes. After slow cooling the tip is cut and broken off so that a plug 5 to 7 mm. long remains in the tube. The end is ground smooth with Carborundum dust and water on a glass plate, washed, dried, and finally fire-polished. The result is a neatly encased plug of sufficient porosity to permit slow liquid diffusion. With the hydrostatic head of the half-cell here described, the plugs used permit the passage of about 0.05 cc. per minute. Plugs of various porosity can be prepared by altering the size of the Pyrex and Alundum particles, and the time and intensity of heating.

The main vessel of the calomel electrode consists of a small Pyrex carbon funnel having a side tube sealed to the stem for mercury connection. A short piece of platinum wire is sealed in the lower end of this side arm to prevent outside contamination of the mercury in the cell. About 3 cm. of heavy-walled rubber tubing is attached to the stem and the porous-tip tube, cut to proper length, is thrust through this into the funnel; the plugged end should extend 4 or 5 cm. below the stem and the open end should be well above the mercury-calomel paste but under the surface of the potassium chloride–calomel solution after the cell is made up. It is essential that the outside diameter of this tube be small enough to permit the mercury of the cell to flow around it in the stem and make contact with the platinum wire in the side arm. At the same time, the inside diameter must be sufficiently large to permit ample cross section of solution

for conductivity. The rubber slip joint is brushed with an alcoholic solution of shellac, wound tightly with a narrow strip of friction tape, and again shellacked. Since this joint must retain mercury, the section of rubber tubing must be live and fit snugly around the smaller glass tube. Shellacking and taping are effective in preventing deterioration. Several such joints have been in service over two years and show no signs of cracking or leaking.

Before assembling the calomel electrode, it is advisable that the various parts, including the rubber slip joint, be thoroughly cleaned and dried. The porous-tip tube may be cleaned with cleaning solution and rinsed with distilled water under pressure. After assembly is made, the vessel is fixed in a clamp and the cell made up in the usual manner, except that precautions to prevent or eliminate air bubbles in the mercury around the tube in the stem and in the potassium chloride–calomel solution in this tube must be observed. Air bubbles in the mercury can be worked out by gently tapping the porous-tip tube on the lower end. If enough potassium chloride–calomel solution is added to cover the opening of the porous-tip tube to a depth of 1 or 2 cm., and if the tube is clean, the solution will slowly force the air down through the tip without formation of air bubbles. Bubbles inadvertently formed may be removed with a fine capillary pipet.

The vessel is finally closed with a short rubber stopper fitted with a glass stopcock and a glass-stoppered separatory funnel or other similar container of about 25 cc. capacity. The stopcock is convenient as an air relief valve, while the separatory funnel is used as a reservoir for potassium chloride–calomel solution. The rubber stopper should fit tightly and should be well shellacked, as the vessel must be air-tight to prevent uncontrolled escape of solution from the tip.

Assembly of Salt Bridge and Cell

The salt bridge, of 7-mm. Pyrex tubing, is made in the form of a low H with inclined cross bar. A 500-cc. separatory funnel connected by 2 feet (0.6 meter) of heavy-walled rubber tubing to the lower end of the higher vertical tube, serves as a reservoir for saturated potassium chloride solution. The tip of the calomel electrode is inserted through a tight rubber connection into the upper end of this tube until it rests in line with the bore of the inclinded cross tube. The lower end of the other vertical tube is fitted with a short piece of rubber tubing and a pinchcock for use as a clean-out. Above this, closely connected by rubber, is a 3- or 4-cm. length of glass tubing the same diameter as the main portion of the bridge, and carrying a smaller sealed-on wash-out tube with stopcock, bent vertically. At the top is a short section of heavy rubber tubing extending 5 mm. beyond the glass. This serves as a slip joint through which the stem of the hydrogen-electrode vessel may be freely but tightly inserted or removed. Construction details are shown in Figures 1 and 2.

The entire apparatus, except the hydrogen-electrode vessel, should be rigidly clamped to a solid support. A large clamp for the hydrogen-electrode vessel should be securely fixed in position so that by slightly loosening the jaws, this vessel may be connected with or removed from the bridge. A view of the apparatus in working position, including the potentiometer system, is given in Figure 3.

All rubber connections should be shellacked and allowed to dry before filling the bridge with saturated potassium chloride solution. If this is done, there will be no trouble with leaks or creeping of salt from the joints.

The reservoir of saturated potassium chloride solution is suspended in a split ring 15 or 20 cm. higher than the liquid level in the calomel half-cell. To fill the bridge, the stopper in the reservoir is loosened and the stopcock partially opened. Air bubbles may be removed by squeezing the rubber connecting tube and manipulating the pinchcock on the clean-out. It is particularly important to eliminate air bubbles about the porous tip of the calomel electrode. If this tip is properly placed as previously described, no air bubbles interfering with conductivity will collect. After the bridge has filled and solution overflowed from the washout, the reservoir stopcock is closed. The apparatus is then ready for connection with the hydrogen electrode.

It should be noted that when the potassium chloride–calomel solution reservoir on the calomel electrode has the stopper loosened and stopcock open, the solution will slowly diffuse through the porous tip into the bridge solution, provided the latter is not under full pressure from its reservoir. This pressure need be exerted only momentarily, as will be apparent from subsequent details of procedure, and a slight flow from the calomel electrode can be maintained as desired. Protection of the solution in this electrode is assured by allowing a short flow every hour during a series of determinations. Approximately 500 determinations may be made before the potassium chloride–calomel solution reservoir requires refilling.

Method of Operation

Procedure in making a determination will vary with the amount of sample. When an ample quantity is available, an amount sufficient to fill the hydrogen-electrode vessel is poured directly into it, after first closing the stopcock and removing the stopper assembly. The latter is then inserted carefully so as to expel all air and excess liquid through the

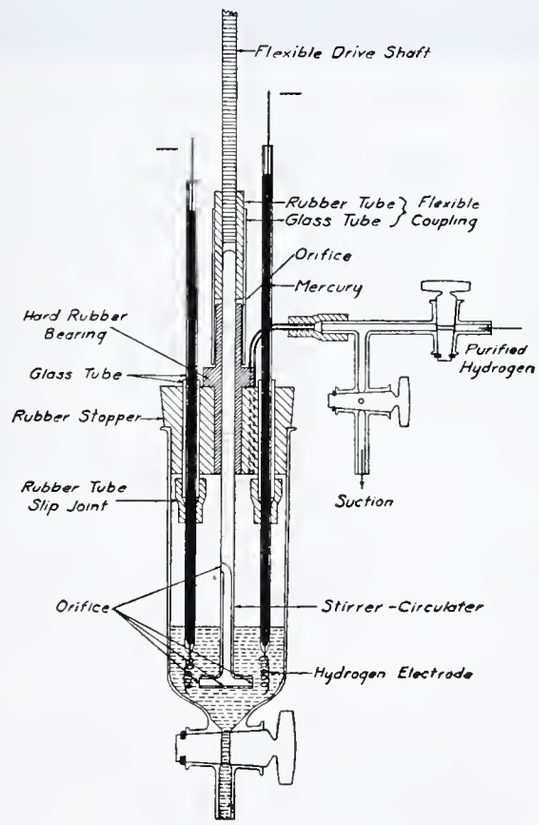


Figure 2—Hydrogen Half-Cell Assembly

hydrogen inlet. The rubber tube supplying purified hydrogen at the rate of approximately 5 cc. per second is then connected with the inlet, after which hydrogen will escape through the release valve consisting of a glass tube connected to a T in the delivery line and opening below the surface of water in a suitable container. By opening the stopcock of the vessel, a stream of liquid is allowed to run out slowly until approximately 20 cc. remain, the balance having been displaced by hydrogen. The stopcock is then closed. During this displacement the rates of the flow of hydrogen and

the escape of liquid should be nearly equal. Such precaution is advisable to prevent accidental entrance of air, although the small quantity of liquid finding its way into the bearing around the stirrer shaft forms an effective seal which will hold pressure much in excess of that permitted by the hydrogen-release valve. This liquid seal is also effective in preventing escape of hydrogen during operation of the stirrer and eliminates a mercury seal. If the period of stirring exceeds 15 or 20 minutes, the bearing may become dry and permit escape of hydrogen; this will be indicated at once by passage of hydrogen bubbles through the washing train. It is then necessary to renew the seal by applying a few drops of water about the shaft at the upper end of the bearing. An orifice in the glass tube of the flexible coupling is provided for this purpose.

Figure 3—Hydrogen-Electrode Cell and Potentiometer System

When the amount of sample is limited or when the solution is strongly acid or alkaline, the hydrogen-electrode vessel is first filled with distilled water, and the water then displaced with hydrogen; the sample, in a shallow container, is then drawn into the vessel through the stem by suction applied at a T in the hydrogen supply line, a small quantity thus introduced being first used as a rinse. This T is fitted with two stopcocks, as shown in Figures 1 and 4, for the obvious manipulations required. Suction is conveniently obtained by controlled siphoning of water from a large bottle. To avoid entrance of air into the vessel, the hydrogen flow is not shut off at the T until the stem is submerged in the sample. Care in using the suction is also essential to prevent drawing in air bubbles with the last traces of liquid. A volume of 8 to 10 cc. is the minimum on which a determination can be made with the size of apparatus described.

Figure 4 shows the position of the hydrogen-release valve and suction bottle in relation to the hydrogen-purifying train.

After the sample has been introduced, the vessel is lowered through its supporting clamp and the stem inserted through the short rubber connection into the bridge with the stopcock of the washout tube open. The clamp is then tightened. Connection with the potentiometer system is made by inserting the proper wires into the mercury leading to the hydrogen electrodes.

The stopcock of the vessel is opened to permit about 1 cc. of liquid to escape over the saturated potassium chloride solution into the washout tube. It is then closed, and the saturated potassium chloride–reservoir stopcock opened slightly to allow potassium chloride solution to sweep out the mixture through the washout tube. While potassium chloride solution is still flowing the stopcock on the washout tube is closed, followed by closing of the potassium chloride–reservoir stopcock. Owing to flexibility of the rubber tube connecting this reservoir with the bridge and to cushioning effect of air pockets in the system, the solution is retained under sufficient pressure so that when the stopcock of the hydrogen-electrode vessel is now opened, the junction between saturated potassium chloride solution and the liquid in the vessel rises 4 or 5 mm. into the stem. This junction is plainly visible and perfectly sharp, and may be reproduced at will.

The flexible drive shaft is connected with the stirrer by swinging the drive shaft bearing into proper position and inserting the driving end into the flexible coupling. After connection has been made, the bearing is raised slightly, adjusted so that the stirrer rotates smoothly, and the motor started. The speed should be so regulated that the stirrer, as it circulates the confined hydrogen, throws a stream of both liquid and gas about the electrodes, and thus rapidly brings about equilibrium.

Following a determination, the stopcock on the hydrogen-electrode vessel is closed, the stopcock on the washout tube opened, and with necessary disconnections made, the vessel is lifted from the bridge, washed with distilled water, and then rinsed with a portion of the next sample preparatory to another run, as previously described. It is unnecessary to remove the stirrer and electrodes from the stopper between each determination for washing.

Operation of the stirrer has no disturbing effect on the liquid junction. This is clearly shown by adding phenolphthalein to sodium hydroxide solution in the hydrogen-electrode vessel and then starting the stirrer; the main body of solution becomes pink almost instantly, but even after prolonged stirring the color will not extend past the open stopcock to the junction in the stem. Pulsation of the junction is avoided by placing the hydrogen-release valve before the wash bottles in the hydrogen supply line.

The stirrer is especially efficacious with solutions which tend to foam badly. As soon as foam rises to the level of the upper orifice in the shaft, it is drawn down through this into the solution again. Changes due to surface phenomena are thus reduced to a minimum.

Five minutes is the average time required for a routine determination, including all incident manipulations.

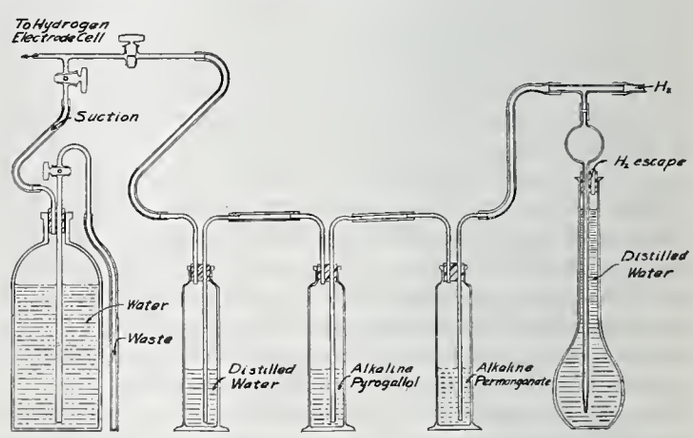


Figure 4—Hydrogen-Purifying Train with Suction Bottle and Release Valve

Use of Standard Half-Cell

A saturated potassium chloride–calomel half-cell was used in all determinations and was checked against a 0.1 N potassium chloride–calomel half-cell from time to time, the average values at various cell temperatures being within 0.5 millivolt of the values given by Clark (*2*). Readings were made with a Leeds & Northrup Type K potentiometer and a No. 2420-c enclosed lamp and scale galvanometer. The entire apparatus was appropriately shielded and housed in an air bath, the temperature of which varied not more than 1° C. during a given set of determinations.

The 0.1 N potassium chloride–calomel half-cell used for checking may be temporarily introduced at the slip joint provided for the hydrogen-electrode vessel. As soon as readings have been made, it is removed and clamped out of the way. The porous tip is washed and flushed, and then kept immersed in some of the half-cell solution in a small protecting test tube held in place by a rubber sleeve above the tip. It is preferable, however, to place the comparison electrode in the system permanently. The tip is inserted

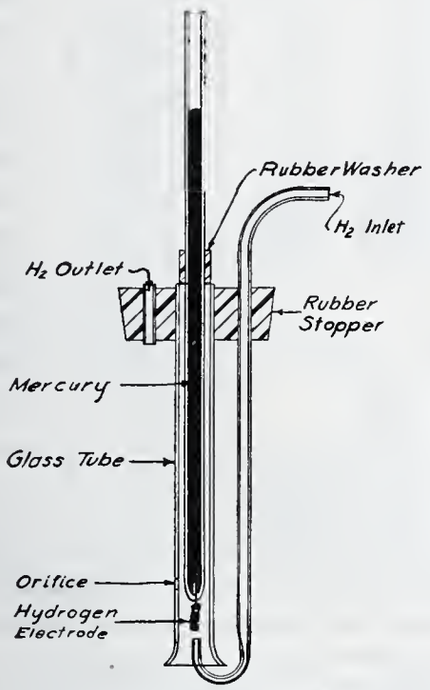


Figure 5—Bubbling Hydrogen Electrode

through a tight rubber connection to a level slightly below the outlet of a T provided near the middle of the bridge. By opening the stopcock on the outlet tube and allowing saturated potassium chloride solution to rise about the porous tip, contact can be established as desired without disturbing the half-cell. Contact should be broken as soon as comparison has been made. This is done by draining off some bridge solution and allowing a protective air bubble to form about the porous tip. The tip may then be flushed in the usual manner to prevent contamination.

The total volume of the various air bubbles or pockets in the complete bridge system should be kept at a minimum, or else the combined cushioning action may produce too high a rise of the liquid junction in the stem of the hydrogen-electrode vessel. Some practice in the various manipulations is required before the desired results may be obtained.

Attainment of H-Ion Equilibrium

As soon as the stirrer is started, the voltage rises rapidly and usually reaches a constant maximum in 1 to 2 minutes. A drift due to junction potential may develop, but by renewing the liquid junction, the original value can be restored. In observations made on 0.05 M potassium acid phthalate solutions during stirring periods of one hour, the voltage varied not more than 0.5 millivolt from the initial maximum attained in less than 2 minutes; with junction renewals the variation was reduced to 0.1 millivolt. Similar results were obtained with various solutions of carbonates and sulfates.

In determinations made on nearly one thousand soil extracts, equilibrium was generally attained within 2 to 3 minutes. Occasionally there occurred serious drifts which could not be obviated by junction renewals. Often the cause was obscure, but in some cases was due to deposition of certain cations on the electrodes. With a series of soil samples carrying traces of zinc, lead, and copper it was found necessary to clean and replate the electrodes for each determination. A saturated solution of copper carbonate in distilled water presented no difficulty, but when the solution was saturated with carbon dioxide in the presence of the solid salt, the increased concentration of cupric ion caused so rapid a deposition that results were not reliable. A similar experience was encountered with press juice of apple leaves. When working with juice from leaves sprayed with lead arsenate, the electrode surface had to be renewed for each determination, while with juice of unsprayed leaves this was not necessary. The hydrogen electrodes were definitely "poisoned" in these instances and would subsequently give decidedly low readings with either duplicates or standard pH solutions.

Smaller drifts were usually evident in all determinations made on a variety of plant extracts. In general, freshly extracted juice gave greater drifts than old material, while samples preserved several weeks with formaldehyde exhibited less than 1 millivolt fluctuation in e. m. f. after the first 2 minutes of stirring. Evidence of poisoning was absent in such cases. Duplicate determinations checked well, and readings on standard solutions were satisfactory. An additional check was made from time to time by repeating the determination on the first sample in a series; if the result obtained after previously running 8 to 10 other samples was in close agreement with the first value, the electrodes were considered to be in good order. Cumulative poisoning or hysteresis may be thus detected, although this phenomenon is generally indicated by the tendency of evento lerable differences between successive duplicate determinations to be in the same direction. Satisfactory performance of a hydrogen electrode is not necessarily indicated by persistence of good duplication of results in orderly series; a better criterion is found in acceptable agreement between duplicates included at random.

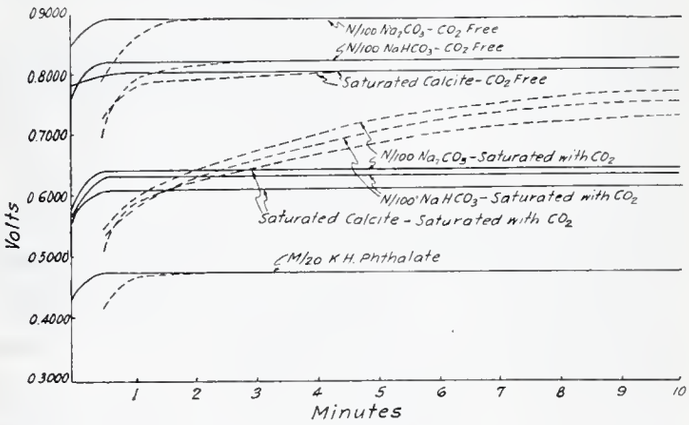


Figure 6—Voltage-Time Curves Obtained with Circulating Hydrogen Electrode and Bubbling Hydrogen Electrode in CO_2–Free and CO_2–Saturated Solutions

Circulating electrode ————
Bubbling electrode — — — —

Drifts which cannot be eliminated by junction renewal may be attributed to reaction between certain sample constituents and hydrogen or the electrode. When these are extensive, the point of H-ion equilibrium is often masked. If the e. m. f. change in such cases be followed closely, there may be obtained a voltage-time curve valuable for interpreting results. A rapid, more or less asymptotic rise during the first 2 or 3 minutes of stirring indicates the progress of hydrogen saturation and reduction of the solution. In the absence of pronounced side reactions in the solution or at the electrodes, the maximum value is subsequently maintained indefinitely and represents the point of true H-ion equilibrium. When incidental reactions alter the original pH, a point of inflection usually occurs in the curve at or near the maximum. In general, the e. m. f. then either falls more or less rapidly or continues to rise more slowly and indefinitely,

Table I—Potentiometer Readings during Typical pH Determinations with Circulating Hydrogen Electrode

Material	Detn.	Minutes from Start of Stirring							One Minute after Stopping Stirrer	Av. of Accepted Values[a]	
		0	0.5	1	2	3	4	5			
		Volts	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*pH*
Soils:[b]											
C10	1	0.7759	0.7974	0.8184	0.8200[a]	0.8191	0.8188		0.8256		
		0.7765	0.7975	0.8193	0.8203[a]	0.8193	0.8189		0.8256	0.8202	9.72
	2	0.7756	0.8003	0.8219[a]	0.8215	0.8214	0.8205	0.8191	0.8257		
		0.7769	0.8001	0.8212[a]	0.8211	0.8205	0.8201	0.8185	0.8255	0.8216	9.75
L4	1	0.5202	0.5710	0.5717[a]	0.5717	0.5711			0.5774		
		0.5190	0.5720	0.5720[a]	0.5720	0.5710			0.5772	0.5719	5.53
	2	0.5135	0.5690	0.5722	0.5722[a]	0.5717			0.5776		
		0.5153	0.5701	0.5721	0.5722[a]	0.5713			0.5776	0.5722	5.53
M2	1	0.4585	0.7117	0.7140[a]	0.7140	0.7135			0.7297		
		0.1995[c]	0.7120	0.7140[a]	0.7140	0.7132			0.7297	0.7140	7.93
	2	0.4705	0.7120	0.7142	0.7143[a]	0.7142			0.7235		
		0.2480[c]	0.7120	0.7145	0.7145[a]	0.7141			0.7235	0.7144	7.94
Apple-leaf press juice, fresh; not sprayed	1	0.5093	0.5397	0.5455[a]	0.5427	0.5421	0.5415		0.5496		
		0.5076	0.5370	0.5450[a]	0.5426	0.5420	0.5413		0.5498	0.5453	5.08
Preserved,[d] sprayed	2	0.5015	0.5315	0.5321	0.5319	0.5319	0.5321[a]	0.5319	0.5362		
		0.4957	0.5313	0.5316	0.5315	0.5317	0.5321[a]	0.5319	0.5360	0.5321	4.85
Iced,[e] sprayed[f]	1	0.4450	0.4870	0.4949	0.5010	0.5056	0.5066	0.5075[a]	0.5302		
		0 4457	0.4876	0.4980	0.5076	0.5090	0.5102	0.5100[a]	0.5318	0.5088	4.46
	2	0.5124	0.5329[a]	0.5315	0.5293	0.5283			0.5385		
		0.5125	0.5320[a]	0.5313	0.5300	0.5293			0.5410	0.5325	4.86
	3	0.4808	0.5177[a]	0.5150	0.5140				0.5404		
		0.4900	0.5240[a]	0.5127	0.5116				0.5424	0.5209	4.66
	4	0.5004	0.5320[a]	0.5308	0.5295	0.5281			0.5414		
		0.5014	0.5324[a]	0.5311	0.5298	0.5286			0.5411	0.5322	4.85
0.02 N H_2SO_4	1	0.3082	0.3531	0.3532[a]	0.3532	0.3532	0.3531		0.3529		
		0.3086	0.3530	0.3532[a]	0.3533	0.3532	0.3532		0.3530	0.3532	1.84
0.02 N H_2SO_4 saturated with CO_2	1	0.3260	0.3463	0.3515[a]	0.3515	0.3514	0.3512		0.3512		
		0.3265	0.3463	0.3515[a]	0.3515	0.3514	0.3512		0.3512	0.3515	1.80
Saturated NaOH soln., CO_2-free	1	1.1735	1.1767	1.1773	1.1782[a]	1.1778	1.1778	1.1767	1.1769		
		1.1687	1.1774	1.1775	1.1783[a]	1.1797	1.1791	1.1776	1.1776	1.1783	15.80
0.05 M KH phthalate[g]	2	0.4394	0.4785	0.4787	0.4788[a]	0.4789	0.4788	0.4788	0.4790		
		0.4410	0.4786	0.4788	0.4788[a]	0.4788	0.4788	0.4789	0.4790	0.4788	3.95

[a] Values accepted as most nearly representing equilibrium with original H-ion concentration.
[b] Determinations made on solutions decanted after shaking 20 grams of air-dry soil with 100 cc. distilled water intermittently for 30 minutes. A second 20-gram portion of each soil was similarly treated for the duplicate determinations.
[c] Second hydrogen electrode was 2 cm. in length; the first, 4 cm. In all other determinations both hydrogen electrodes were approximately 4 cm. in length.
[d] Sample preserved with 0.1 per cent formalin for 30 days. Leaves sprayed once with lead arsenate.
[e] Sample frozen as soon as collected; thawed 4 days later and tested when at room temperature. Leaves sprayed 3 times with lead arsenate.
[f] Determinations made on separate portions of same sample. Electrodes used for first determination had just previously been used on two other samples from heavily sprayed leaves. Electrodes replated and checked for second and fourth determinations.
[g] Determination made immediately following preceding determination on saturated NaOH solution after rinsing vessel and electrodes with 3 portions of the phthalate solution, stopper assembly remaining in place.

according to the nature of the incidental reactions. The pH corresponding to the e. m. f. at such inflections is regarded as a closer approach to the original than a pH based on so-called constant e. m. f. values which may appear later. If a constant value is not attained within 2 or 3 minutes, or if subsequent changes are due to causes other than junction potential, an apparently constant value obtained much later will usually be revealed by extended observation as a point in a retarded phase of drift. This is because electrode-poisoning phenomena and alteration of the original pH of the solution by contact with hydrogen or the hydrogen electrode are often relatively slow reactions.

Rigid limits of tolerance for variation between duplicate determinations can be satisfied in cases of rapidly attained constant readings. The limits need be little less rigid when inflections in voltage-time curves are used.

Discussion of Results

Typical examples of voltage changes during determinations on various samples are presented in Table I. The general course of e. m. f. during a determination with the stirring electrode is shown to be a rapid rise during the first 0.5 minute, after which the rate of increase falls off sharply until a maximum value is reached. This maximum e. m. f. is regarded as concurrent with the desired hydrion equilibrium and is used for calculating the original pH of the solution. It usually persists for less than 1 minute, generally being promptly followed by a more or less rapid drop. Exceptions occur with certain biological materials, of which seminal fluid is a striking example. As illustrated in Table II, this gives an e. m. f.–time curve showing a rapid rise and approach to a nearly maximum value, after which a gradual but persistent rise continues indefinitely. The point of inflection marking the beginning of the gradual rise is selected as the value most nearly coincident with equilibrium involving the original H-ion concentration. Side reactions during pH determinations with the hydrogen electrode are of general occurrence. Their inevitable influence on the original pH can be reduced to a minimum by a most rapid hydrogen saturation to effect H-ion equilibrium, and on this basis is justified the calculation of pH from the rapidly attained maximum or inflection e. m. f. value as just described. A constant e. m. f. or static equilibrium was rarely found except with certain simple solutions, such as 0.05 M potassium acid phthalate and 0.02 N sulfuric acid. This is not surprising in view of the high catalytic activity of the hydrogen electrode, and with the stirring electrode a constant e. m. f. need not be required as a criterion of reliability.

In each determination where the hydrogen electrodes functioned normally, they agreed within less than 1 millivolt at the promptly attained equilibrium. Greater variation than 1 millivolt between the two at equilibrium, or slow attainment of equilibrium, or both, generally was associated with electrode poisoning. This is well illustrated by the data given for apple-leaf press juice. Equilibrium between normally functioning electrodes and 0.05 M potassium acid phthalate was invariably attained after 1 to 2 minutes of stirring. Values of 0.4780 to 0.4820 volt were obtained under temperature and pressure conditions ranging from 20° to 32° C. and 670 to 720 mm. mercury. The time required for equilibrium with other solutions varied from 0.5 to 4 minutes. An observation period of not more than 5 minutes was sufficient, therefore, to determine the point of H-ion equilibrium in any case.

Additional data in Table II include results obtained with

Table II—Comparison of Voltage Change during pH Determinations by Bubbling and Circulating Hydrogen Electrodes

Sample	Minutes from Start of Stirring or Bubbling									One Minute after Stopping Stirring or Bubbling	Av. of Accepted Values[a]	
	0	0.5	1	2	3	4	5	6	10			
	Volt	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*pH*
Soils:[g]												
C10[b]	[c]	0.7000	0.7677	0.8162	0.8241	0.8270	0.8281	0.8283[a]	0.8278	0.8301	0.8283	9.86
C10[d]	0.8030	0.8245[a]	0.8240	0.8231	0.8222	0.8220				0.8258		
	0.8017	0.8245[a]	0.8238	0.8225	0.8221	0.8215				0.8258	0.8245	9.80
E7	....	0.5052	0.5752	0.6290	0.6501	0.6590	0.6644	0.6683	0.6740	0.6802	?	?
E7[d]	0.6050	0.6580	0.6675	0.6700	0.6711[a]	0.6711	0.6707	0.6701		0.6718		
	0.6051	0.6584	0.6678	0.6702	0.6712[a]	0.6711	0.6708	0.6703		0.6718	0.6712	7.21
E7[e]	0.5830	0.6404	0.6508	0.6535	0.6551	0.6554[a]	0.6551	0.6544		0.6563		
	0.5780	0.6405	0.6508	0.6538	0.6555	0.6555[a]	0.6555	0.6548		0.6571	0.6555	6.94
F22	....	0.3101	0.6867	0.7244	0.7365	0.7388	0.7415	0.7447[a]	0.7432	0.7442	0.7447	8.45
F22[d]	0.7148	0.7424	0.7433[a]	0.7433	0.7430					0.7438		
	0.7169	0.7425	0.7435[a]	0.7435	0.7431					0.7438	0.7434	8.43
F22[e]	0.6812	0.7358	0.7377	0.7392	0.7394[a]	0.7395	0.7390			0.7434		
	0.6819	0.7362	0.7380	0.7394	0.7395[a]	0.7395	0.7389			0.7439	0.7395	8.36
Seminal fluid:												
Duroc boar 1	0.6624	0.6813	0.6855	0.6860[a]	0.6862	0.6865	0.6869	0.6871	0.6880	0.6884		
	0.6664	0.6845	0.6863	0.6870[a]	0.6875	0.6880	0.6888	0.6889	0.6899	0.6904	0.6865	7.47
Duroc boar 1[f]	0.6005	0.6016	0.6730	0.6872	0.7005	0.7120	0.7190	0.7222	0.7290	0.7325	?	?

[a] Values accepted as most nearly representing equilibrium with original H-ion concentration.
[b] Compare with data for C10 in Table I.
[c] Only one hydrogen electrode used in bubbling vessel.
[d] Solution used in preceding determination transferred to stirring-electrode vessel.
[e] Determination on separate portion of same soil extract used for two preceding runs.
[f] Sample from stirring-electrode vessel transferred to bubbling vessel.
[g] For analysis of soils see Table III.

a bubbling hydrogen electrode constructed as shown in Figure 5 and used in the stirring-electrode vessel. More time was always required for the bubbling cell to bring about equilibrium, although hydrogen was bubbled at a maximum rate and efficient circulation of solution was obtained. In no case was equilibrium attained in less than 6 minutes, and in numerous instances it was not reached in 10 minutes. Not infrequently soil extracts and biological fluids were encountered that apparently could not be brought to equilibrium with the bubbling electrode, the e. m. f. continuing to rise during periods of bubbling as long as 4 hours. Since junction potentials and electrode poisoning were eliminated as contributing factors to such pronounced drifts, they can be attributed to slow side reactions. With potassium acid-phthalate solutions, prepared with ordinary distilled water, the values obtained were approximately 1 millivolt higher than those given by the stirring electrode under the same conditions. This increase was due to removal of dissolved carbon dioxide by the escaping hydrogen. Values obtained on carbon dioxide-free phthalate solution in the stirring cell were identical with values secured on either carbon dioxide-free or carbon dioxide-saturated phthalate solutions with the bubbling hydrogen electrode. Similar results were obtained with other acid solutions.

The different behavior of the stirring and bubbling hydrogen electrodes is shown graphically in Figure 6. Only when solutions are free of carbon dioxide do both methods give like values; the greater the carbon dioxide content the greater the divergence in results. The greater rapidity of the stirring electrode in all cases is also illustrated. Most significant, however, is the evidence that when appreciable amounts of carbon dioxide are present in solution, it is impossible even to approximate the original pH value with the bubbling hydrogen electrode. If bubbling were continued long enough to remove all dissolved carbon dioxide, and if no irreversible reactions were involved, the pH finally reached would be the same as that of the original carbon dioxide-free solution. An attempt was made to realize this experimentally with the carbon dioxide-saturated carbonate solutions. As the curves indicate, sufficient carbon dioxide was removed in 10 minutes to increase the pH approximately 2 units, but further observation showed that the rate of increase became gradually slower so that after 2 hours the e. m. f., although apparently constant, had not yet reached the maximum.

The effect of the bubbling electrode is further emphasized by differences obtained when a determination is repeated on the same portion of sample by the stirring electrode, and vice versa. This is illustrated with each sample in Table II

Table III—Analyses of 1:5 Water Extracts of Soils Used for Data in Table II

Soil	Equivalent Parts per Million of Solution[a]											
	SiO_3	CO_3	HCO_3	SO_4	NO_3	Cl	Fe	Al	Ca	Mg	Na	K
C10	6.6	9.6	18.8	2.0	0.1	0.7	0.7	0.0	0.0	0.0	12.3	12.1
E11	0.6	0.0	1.6	0.1	0.2	0.0	0.4	0.3	0.4	0.1	0.1	0.5
F22	0.6	0.0	0.9	0.1	0.1	0.0	0.0	0.0	0.8	0.2	0.6	0.2

[a] Equivalent p. p. m. = p. p. m. $\times \frac{1}{\text{equivalent weight}}$. For discussion of this method of expression see Bollen and Neidig, *Soil Science*, **24**, 69–70 (1927).

Values recorded under zero time from start of stirring or bubbling indicate that during introduction of a sample into the stirring-electrode vessel, there occurs sufficient contact with hydrogen to give an e. m. f. not much less than the equilibrium value. This preliminary e. m. f. is more or less unstable, tending to increase slowly and fluctuating in proportion to current withdrawal during potentiometric balancing. The bubbling electrode gave no e. m. f. before hydrogen was allowed to flow. On discontinuing either stirring or bubbling, however, there usually developed an e. m. f. distinctly higher than any preceding value. This generally reached a relatively constant maximum in about 1 minute, although the extent and duration of increase were found to vary with the nature of the solution and condition of the electrodes. It is noteworthy that the length of the hydrogen electrode influenced only preliminary e. m. f., as is shown by the data for soil M2 in Table I. The initial and final readings in the various examples are presented as a matter of interest. In routine determinations it is sufficient to follow the e. m. f. closely only in the region of equilibrium.

Literature Cited

(1) Clark, "Determination of Hydrogen Ions," p. 286, Williams & Wilkins, 1928.
(2) Clark, *Ibid.*, p. 488.
(3) Clark, *J. Biol. Chem.*, **23**, 475–86 (1915).
(4) Parker and Dannerth, Ind. Eng. Chem., **17**, 637–9 (1925).
(5) Schollenberger, *Ibid.*, **17**, 649 (1925).
(6) Snyder, U. S. Dept. Agr., *Circ.* **56** (1928).
(7) Waterman, *J. Assocn. Official Agr. Chem.*, **10**, 390–5 (1927).

Method for Identification of the Common Gums[1]

Morris B. Jacobs and Leon Jaffe

Department of Health, 505 Pearl St., New York, N. Y.

A method for the identification of gums by the use of group reagents is outlined. It is shown that the manner of solubility of a gum may be used as an indication of the gum. The specific characteristic tests of the gums are emphasized and a table of the reactions of the gums appended so that the test for a given gum may be seen at a glance.

In recent years many new products of a gum-like nature have been put into use in place of acacia, tragacanth, and the like. These pectinous bodies have not as yet been investigated although there is a growing need for methods for their identification. They have, of course, some properties which distinguish them from like substances and consequently enable them to be detected. This paper gives the results of an investigation of these properties. For the sake not only of completeness but also of usefulness, the tests for the older known gums have been included, and many new ones which our investigation has disclosed have been added. An analytical method for the identification of these gums has also been developed.

The few methods for the separation of gums from foods, drugs, cosmetics, etc., that are found in the literature are of little value and do not lend themselves to use for identification purposes. That of Cook and Woodman (*2*) was used by the authors in some cases.

The methods proposed are all rapid methods and involve no need of hydrolysis of the gum and then subsequent identification of the hydrolysis products, a procedure which, for a commercial laboratory, where these methods will probably find their greatest use, is too long-winded and thus of no practical value.

Patrick (*3*) proposed a method for the detection of thickeners in ice cream, satisfactory for the detection of thickeners as a group, but not providing for identification. The use of hydrochloric acid in this method, to dissolve excess milk proteins, interferes with the characteristic reactions of the gums.

Cook and Woodman (*2*) give a method not only for the separation of gums but also for the identification of some of them by an alcohol-precipitation method. Theirs has the disadvantage of the use of tannic acid as a precipitant for the protein bodies in the product from which the gum is being extracted, which not only precipitates the proteins but some part of the gums as well. For example, it precipitates locust kernel, quince seed, and Hull emulsifier.

Weinberger and Jacobs (*5*) published a method for the identification of gums by means of a characteristic alcohol precipitate. This method is in itself insufficient to identify some of them positively and does not include some of the newer gum products.

Congdon's method (*1*), as pointed out by Cook and Woodman, is practically useless because the tests are applied without prior separation of the gums, and consequently the tests are often performed on impurities in the gums. Furthermore, if the gum happens to be incorporated in a food, drug, or cosmetic, the characteristic reactions may be entirely masked.

Revis and Bolton (*4*) give a method for the separation and detection of agar-agar which is in reality a general one for the detection of gums as a group rather than for agar-agar alone because they rely on the jellying action of a concentrated solution of agar as the test.

The gums may be extracted from foods, drugs, and like substances by the method either of Patrick or of Cook and Woodman. The Patrick (*3*) method is essentially as follows: To the sample containing the gum, add half its volume of water and boil for a few minutes. Then add 2 cc. of 10 per cent acetic acid for every 50 cc. of sample, heat to boiling, and add 3 teaspoonfuls of kieselguhr for every 50 cc. of the sample. Filter on a plaited filter and discard the precipitate. Precipitate the gum from the filtrate by the addition of 12 cc. of 95 per cent alcohol for every 3 cc. of the filtrate. Add 3 cc. of a mixture of 95 cc. of 95 per cent alcohol and 5 cc. of concentrated hydrochloric acid. The acidified alcohol completely dissolves the milk proteins. At this point the authors centrifuged and filtered the alcohol solution containing the precipitated gum, washed the gum with 95 per cent alcohol to free it from the acid, and then allowed the gum to dry spontaneously before applying qualitative tests for its identification.

In the Cook and Woodman (*2*) method, dilute the sample to a suitable concentration with water. Add 5 cc. of dilute acetic acid and 25 cc. of 10 per cent tannin solution, heat the mixture for 20 to 30 minutes, centrifuge, filter, and discard the precipitate. Add 40 to 50 cc. more of tannin solution, heat for a short time, centrifuge, and filter. Again discard the precipitate. Treat the filtrate with twice its volume of acetone. Centrifuge and filter, and discard the filtrate. Dissolve the precipitate in 50 cc. of warm water slightly acidified with acetic acid, and then add 10 cc. of ammonia (sp. gr. 0.90), centrifuge, and filter. Add acetic acid to the filtrate until slightly acid and precipitate the gum with 95 per cent alcohol. At this point the authors centrifuged, filtered, and washed the precipitate with 95 per cent alcohol, and then allowed the gum to dry spontaneously before making qualitative tests.

Table I—Materials Used

Gum	No. and Form of Samples		Test Soln. %	Manner of Solution
Arabic: acacia, arabin	1 3	Powder Lump	1	Goes readily into clear soln.
Tragacanth: bassorin, tragacanthin	2	Powder	1	Swells when placed in water and forms translucent somewhat viscous soln. which becomes ropy on standing
Agar-agar	2	Strip form	0.5	Goes into soln. on warming and on cooling forms gel
Karaya: Indian gum	1 1	Powder Lump	1	Not very soluble in water. Particles swell and form layer at bottom of container
Irish moss: algin	2	Seaweed	0.5 approx.	Translucent, viscous, yellowish soln.
Quince seed	2	Seed	1	Opalescent soln. and stringy precipitate on standing
Locust kernel: locust bean, galagum, lactox	5 1	Powder Extracted from a food	1	Does not form a clear soln. Swells considerably forming opaque colloidal soln. from which flocculent precipitate settles on standing
Hull emulsifier	1	Powder	1	Not very soluble. Particles swell and remain at bottom like Indian gum

In products which contain no alcohol-insoluble substances, such as proteins, dextrins, etc., other than gums, it is best

[1] Received December 8, 1930.

Table II—Results of Tests in Various Gums

Gum	Millon's Reagent	Neutral Lead Acetate 20% Soln.	Basic Lead Acetate (A. O. A. C.)	Potassium Hydroxide 10% Soln.	Neutral Ferric Chloride 5% Soln.	Alcohol Precipitate	Borax, 4% Soln.	Schiff's Reagent	Schweitzer's Reagent	Iodine Soln.	Tannic Acid, 10% Soln.	Sulfuric Acid, Conc.
Arabic	White, fine, opaque ppt., sol. in excess of reagent	No ppt.	White, curdy ppt., insol. in excess	Faint yellow tinge	Ppt. sol. in excess	Very fine floc., non-adherent, 40 cc. pt. of definite pptn.	Negative	Negative	Negative	Negative	Negative	Negative
Tragacanth	Voluminous flocculent translucent ppt.	Voluminous flocculent ppt., gels	Voluminous ppt., gels	Bright yellow, stringy ppt.	Gelatinizes	Coag. long and stringy, adherent, 10 cc.	Negative	Negative	Stringy ppt. on heating	Blue	Negative	Stringy ppt. on heating
Agar-agar	Gelatinizes	Flocculent ppt., gels	Voluminous ppt.	Clarifies soln.	Gelatinizes, heat + excess ⟶ ppt.	Heavy floc., adherent to beaker, 20 cc.	Negative	Negative	Negative	Negative	Negative	Clarifies soln.
Karaya[a]	White, curdy ppt. settles rapidly	Negative	Stringy ppt., settles rapidly	Negative	Ppt. coag. on heating	Fine filamentous particles, non-adherent, 15–20 cc.	Negative	Negative	Negative	Negative	Ppt.	Ppt.
Irish moss	Gelatinizes	Flocculent ppt., gels	Voluminous flocculent ppt., gels	Gels	Vol., stringy ppt., gels	Coagulated, translucent, stringy, adherent, 20 cc.	Negative	Negative	Negative	Negative	Negative	Negative
Quince seed	Voluminous flocculent yellowish ppt.	Yellowish flocculent ppt., gels	Yellowish vol., flocculent ppt., gels	Stringy ppt.	Stringy ppt.	Coag., short, stringy, non-adherent, 25 cc.	Negative	Stringy ppt.	Stringy ppt. on heating	Negative	Ppt.	Stringy ppt.
Locust kernel	Gelatinizes	Voluminous ppt., gels	Gels	Slight floc., ppt.	Stringy ppt.	Stringy, clotty, opaque, non-ad., start, 2 cc., complete, 15 cc.	Gels	Negative	Negative	Negative	Ppt.	Ppt.
Hull emulsifier	Stringy ppt., settles on standing	Small, opaque flocculent ppt.	Flocculent opaque ppt.	Clarifies soln.	Ppt.	Fine floc.; start, 2 cc., complete, 25 cc.	Negative	Negative	Clarifies soln.	Blue	Ppt.	Ppt.

[a] Pink with concentrated phosphoric and hydrochloric acids.

to precipitate the gums directly. If the sample be liquid, merely add the requisite amount of 95 per cent alcohol. If it be solid, add a suitable amount of water, make slightly acid with acetic acid, boil, and filter. Precipitate the gums from the filtrate with 95 per cent alcohol.

Procedure

A list of the gums tested, together with their manner of dissolving in water, is given in Table I. For Irish moss, locust kernel, quince seed, tragacanth, and karaya, a Cook and Woodman extraction of the original test solution and a new test solution were made with the precipitate from the alcohol treatment. These solutions were then subjected to the same tests. They gave corresponding results.

The reagents used were C. P. materials and were made according to directions given in standard texts such as the U. S. Pharmacopeia, the methods of the A. O. A. C., Cohen's Organic Chemistry, etc.

The procedure was, in general, to add 2 or 3 drops of the reagent to 5 cc. of the test solution, note the result, and then add an excess of the reagent. In the case of potassium hydroxide, sulfuric acid, phosphoric acid, hydrochloric acid, Schweitzer's reagent, and neutral ferric chloride, a few drops of the reagent were added to the test solution and the mixture then boiled. Then an excess of the reagent was added and again the mixture was boiled. In the case of Schiff's reagent, the test solution was boiled first and then the reagent added. In each case for this reagent a pink coloration was obtained. This is to be disregarded and only a precipitate formation noticed. For the tannic acid test, dilute acetic acid must be added to the test solution first, and then the reagent added. For the alcohol precipitate, the method of Weinberger and Jacobs was used. For every test, a blank or control must be used in order to distinguish any change in the test solution due to the addition of the reagent.

The results of these tests are given in Table II.

In order to make use of the table properly, care must be taken to notice the distinguishing characteristics of the precipitate formed. That is, whether it is voluminous, flocculent, small flocculent, stringy, powdery, curdy, filamentous, etc. With certain reagents there is no apparent change, hence the use of blanks and controls is essential. The word "gel" in the table indicates an actual jellied condition. When we use the word "gelatinizes" we imply that the mixture has been thickened. These are clear distinctions and are readily noticeable in making the tests.

It will be seen from the above that the table is a means of distinguishing one gum from another. An outline method for the identification of the gums dealt with in this paper, using two reagents and at the most three, is given below. The procedure is as follows: Take 3 cc. of the unknown test solution, add 0.5 cc. of Millon's reagent, and after 5 minutes note the result. This will divide the gums into four groups. Note the group to which the unknown belongs, and again take 3 cc. of the test solution and add the group reagent. This will distinguish the gum. Then make any of the verification tests on 3 cc. of the test solution again, if necessary.

The unknown may be arabic, tragacanth, agar, karaya, Irish moss, quince seed, locust kernel, or Hull emulsifier.

To 3 cc. of unknown test soln. add 0.5 cc. of Millon's reagent:

Group 1	Group 2	Group 3	Group 4
Gelatinizes	Vol. floc. ppt., does not settle	Stringy ppt., settles	Powdery or fine curdy ppt.
Irish moss Agar Locust kernel	Quince seed Tragacanth	Hull emul. Galagum	Arabic Karaya

To 3 cc. of the unknown test soln. add group reagent:

Group 1	Group 2	Group 3	Group 4
Add borax, 4%	Add KOH	Add borax, 4%	Add phosphoric acid
Locust kernel gels Others neg.	Tragacanth, bright yellow Quince seed, stringy ppt.	Galagum gels Hull emul. dissolves in Schweitzer's reagent	Karaya turns pink Arabic dissolves in excess of Millon's reagent

To 3 cc. of test soln. add KOH:

Irish moss gels
Agar soln. clarifies

Notes

Indian gum will give a pink coloration when boiled with either phosphoric or hydrochloric acid. When allowed to stand in either solid or solution form, karaya develops an acetic acid odor.

Quince seed will give a stringy precipitate, which rises to the top with Schiff's reagent.

Hull emulsifier is rendered completely soluble by boiling with potassium hydroxide.

Agar-agar solution is clarified by boiling with concentrated sulfuric acid.

Irish moss smells like seaweed and is jelled by potassium hydroxide.

Tragacanth gives a bright yellow solution and stringy precipitate when boiled with potassium hydroxide solution.

Locust bean may be distinguished from locust kernel by the addition of iodine solution. The former is colored purplish. Galagum may be distinguished from both of these by the stringy precipitate with Millon's reagent.

Each gum has its own peculiar method of going into solution in water. This peculiarity may be sufficient, if one often works with gums, to give an index as to the gum.

Acknowledgment

The authors wish to thank Walter Weinberger for the use of some of his data in the above work.

This work was done in the laboratories of the Department of Health of New York City.

Literature Cited

(1) Congdon, J. Ind. Eng. Chem., **7**, 606 (1915).
(2) Cook and Woodman, *Ibid.*, **10**, 530 (1918).
(3) Patrick, U. S. Dept. Agr., Bur. Chem., *Bull.* **116**, 26 (1914).
(4) Revis and Bolton, "Allen's Commercial Organic Analysis," Vol. VIII, p. 193, Blakiston, 1914.
(5) Weinberger and Jacobs, *J. Am. Pharm. Assocn.*, **18**, 34 (1929).

Accurate Air Separator for Fine Powders[1]

Paul S. Roller

Nonmetallic Minerals Experiment Station, U. S. Bureau of Mines, New Brunswick, N. J.

An apparatus is described for separating quantitatively a 1-kg. charge of fine powder into a series of fractions beginning 0–2.5 microns in size. Except for the finest fractions, at or below 5 microns, where attrition by the air current takes place in the case of soft powders, the particle sizes separated are very homogeneous within the limits given by Stokes' law.

Several causes affect the rate of separation, but the most important is that of the rate of air flow. Under similar conditions the rate of separation is proportional to the air flow. Depending on the latter, initial rates of separation of the particle-size fractions have been made up to 135 grams per hour at a flow of 140 liters per minute.

Continuous separation can be effected by the use of an offset separator tube with separate collection of the oversize. At a 30-micron particle size cut of a Portland cement powder, with an air flow of 500 liters per minute, the equivalent rate of feed was 5.4 kg. per hour, while the rate of recovery was 0.92 kg. per hour. The efficiency of recovery, based on the maximum possible recovery in a run, was not in excess of 28 per cent.

The properties of microscopic powders[2] are greatly dependent on their mean particle size and distribution of sizes. An air analyzer has been described (*2*) for determining the percentage in a microscopic powder of the successive fractions[3] 0–5, 5–10, 10–20, 20–40, 40–60, and > 60 microns. This apparatus operated on a sample of between 25 and 30 grams.

For rapidity and accuracy in analyzing a microscopic powder for its distribution of particle sizes, such a small sample is desirable. However, numerous instances arise when large quantities of each of the particle-size fractions are wanted in order to determine their particular physical and chemical properties; one may also require large quantities below a minimum particle size of, for example, 30 microns. In order to study further the properties of fine particles of natural anhydrite in connection with the retardation of Portland cement, considerable quantities of each of the various fractions were required. It was decided to reconstruct the air analyzer previously described so that a large amount of material could be started with, thus conveniently permitting a large air flow and consequent rapid rate of separation.

Description of Apparatus

In basing the design of the separator on the air analyzer, it was particularly desired to duplicate the self-circulation of the powder charge as illustrated in Figure 1. This figure shows that the particles composing the powder charge circulate in a clockwise direction; at the same time, the whole mass builds up in a direction opposite that of the incoming air. Thus the powder charge is adequately prepared for the air separation. It was soon found with the larger apparatus that the condition of self-circulation of the powder charge was easily attained.

Figure 2 is a photograph and Figure 3 a drawing of the air separator which has been successfully operated over a long period of time.

Container *C* holds about 1 kg. of powder charge. It is a standard 7.6-cm. (3-inch) iron U-bend, with a radius of 11.4 cm. ($4^1/_2$ inches). At the bottom is a plug for emptying this container conveniently. The hard rubber cam shown in the figure rotates at about 300 r. p. m. and operates against a ball-bearing bicycle hub that is fastened to container *C*. The rotation of the cam causes *C* to oscillate about the bearing *B*. The lug *L* is riveted to *C*, and on the upward stroke rises about 1 cm. The downward stroke is accelerated by spring

[1] Received January 20, 1931. Published by permission of the Director, U. S. Bureau of Mines, and not subject to copyright.

[2] A microscopic powder is defined as that portion passing through the 200-mesh sieve.

[3] In making an analysis into six fractions, it has subsequently been found that there is no loss of accuracy, but rather that the time required may be very considerably reduced by using the same separator tube for the 10-micron as for the 5-micron separation. The smaller separator tubes are then employed at the higher rate of air flow for the successive fractions beginning 20 microns. Opportunity is also taken to remark on the microscopic examination of the fractions. It has been found time-saving and more efficient to conclude the dry dispersion of the grains with a grounded platinum wire as described by a similar wet dispersion after the addition of a drop of liquid.

S, via the arm R, acting on lug L. The complete oscillation of container C is abruptly halted in a horizontal plane by impact of lug L against the abutment A. The combined set of forces and reactions causes a circulation of the powder charge as illustrated in Figure 1.

The air enters at I by way of a rubber hose through a brass tube bent concentric with container C and into the end of which screws any one of a set of nozzles, 1 to 14 mm. in diameter. As already noted, the air flow is opposite in direction to that in which the powder charge builds up for self-circulation.

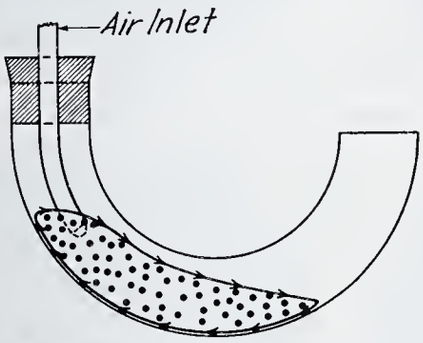


Figure 1—Self-Circulation of Powder Charge

Above bearing B of container C, a piece of rubber inner tube connects by a set of flanges with gasket to separator tube T, made of sheet monel and carefully grounded electrically. In these experiments a set of separator tubes, 7.6, 15.2, 30.4, and 60.8 cm. in diameter, was used. These tubes revolve about a central post and can be successively brought into connection with container C. The cylindrical portion of separator tube T in these experiments was about 31 cm. tall and tapered over the same length (except for the 60.8-cm. tube that was tapered over 45 cm.) to the 7.6-cm. (3-inch) nipple and flange leading to container C.

G is a filter which is connected to separator T by a brass gooseneck with flanged screw cap.

Size of Particle Separated

In conducting a series of separations, the size of separated particle is controlled by the terminal velocity of the air in the separator tubes. Three other factors, the length of separator tube, the inlet nozzle size, and incomplete separation, may affect the accuracy of a fractionation. If the separator tube is too short, the desired equilibrium velocity of the air will not be attained therein, causing the separation of oversize; if the nozzle is too small, the grains may be disrupted into fine particles that are carried over by the air; finally, incomplete separation will show up as undersize in the next fraction.

Defining the diameter of a grain as the arithmetic mean of the length, breadth, and depth (or more conveniently but less accurately, of the length and breadth), it was found by experiment (*2*) that the size of particle separated is related closely to the velocity of the air, in accordance with Stokes' law. Consequently, this law is used as a guide in effecting the various particle-size separations. Stokes' law, which was derived for small falling spheres, is:

$$v = \frac{10^{-8}}{18} g \frac{\rho d^2}{\eta} \qquad (1)$$

where v = terminal velocity of fall in cm. per sec. in stationary fluid
g = constant of gravitation in c. g. s. units
ρ = density of particles in gram per cc.
η = viscosity of fluid in c. g. s. units
d = diameter of sphere in microns (1 micron = 10^{-4} cm.)

Taking $\eta = 1.82 \times 10^{-4}$ at 20° C. for air (*1*), a table like Table I may be constructed for the velocity of fall in air against particle size.

Table I—Velocity of Fall in Still Air of Spherical Particle Calculated from Stokes' Law

Diameter	Ratio Velocity of Fall to Density	Velocity of Fall for Cement (ρ = 3.1)
Microns	*Cm./sec./ρ*	*Cm./sec.*
2.5	0.0185	0.0572
5	0.0740	0.229
10	0.296	0.917
15	0.665	2.06
20	1.182	3.66
30	2.66	8.24
40	4.73	14.65
60	10.62	33.0

Table I has been constructed from Equation 1.

By employing an air flow such that the velocity in the separator tube corresponds to a given particle diameter (Equation 1 or Table I), all particle sizes below the particle diameter in question will be separated. A series of separations may thus be effected so that a set of particle-size fractions is obtained.

Experimentally, it was found on both soft and hard materials that the separations effected with the 1-kg. air separator described above were quite as homogeneous and accurate as with the air analyzer (*2*). Figure 4 is a set of photomicrographs of a series of Portland cement fractions previously reported (*2*) and represents the results obtained on Portland cement with the new air separator. Figure 5 is a set of photomicrographs of a series of fractions, beginning 0–2.5 microns, obtained with the air separator on a finely ground anhydrite. Except for a small amount of undersize within a few microns, due principally to insufficient time for complete separation, the fractions are seen to be pure in the particle-size range delimited by Stokes' law. However, one fraction, 2.5–5 microns, of the anhydrite is contaminated with 0–2.5 micron particles, owing to attrition of the soft powder by the high-velocity air at the inlet.

Figure 2—Assembly of Air Separator

Rate of Separation

Principally it is (1) the rate of air flow that controls the rate of separation. Other factors are (2) the size of inlet nozzle, (3) the concentration in the powder of the fraction separated, (4) nature of the powder, and (5) size of particle separated.

Owing to the operation of factors (2) to (5), the relation between the initial rate of separation and the rate of air flow is somewhat variable. Numerous experiments indicate, however, that under similar conditions the two rates are directly proportional. Approximately the same proportionality applies to different powders and different particle sizes at the same concentration.

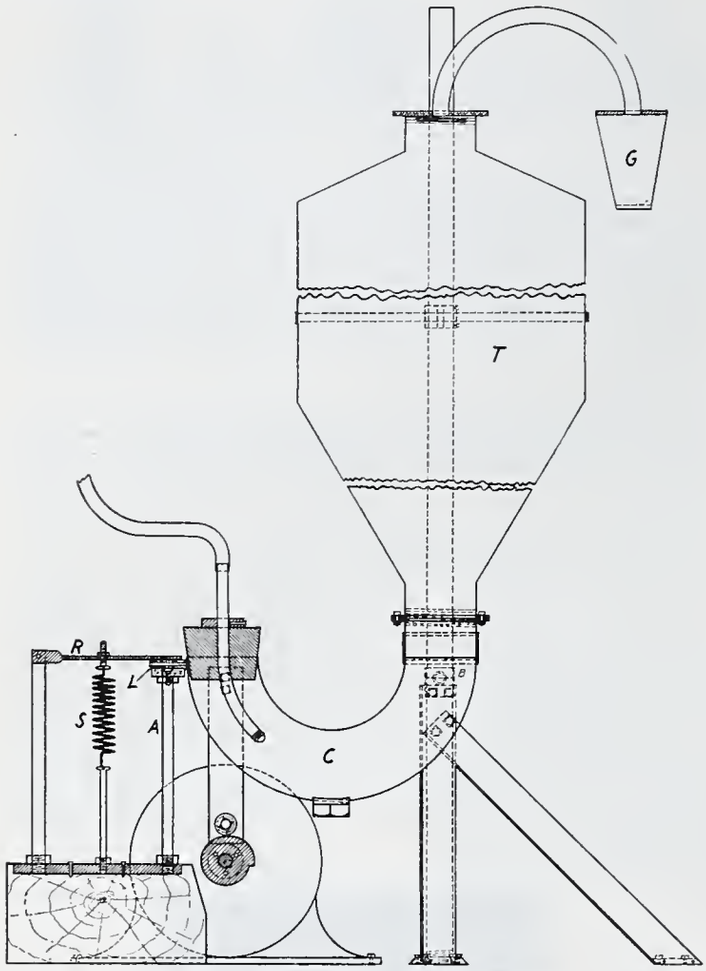


Figure 3—Air Separator, Vertical Section

Since the air velocity in the separator tube controls the size of particle separated, it is clear that the rate of separation is chiefly determined by the size of separator tube, and, indeed, roughly as the square of the diameter. The use of a series of tubes of diameters in the ratio 1:2:4:8 permits the separation of a corresponding series of particle-size fractions at a convenient constant rate of air flow.

With regard to the other factors that affect the rate of separation, it was found that at a given rate of air flow there exists an optimum size of inlet nozzle for securing the maximum rate of separation of each of the fractions. For separations above 5 microns, a ratio of approximately 0.7 to 1 of liters of air per minute to nozzle diameter squared in sq. mm. seems to be best. At and below 5 microns, a suitable fine jet is necessary to overcome the high electrostatic forces between the grains.

Corresponding to the effect of decrease of concentration in the powder of a given fraction, the rate of separation falls off exponentially with time, rapidly at first, then slowly approaching a zero rate, except, in the case of soft powders, for fractions at or below 5 microns where the end rate coincides with a constant rate of attrition.

Operation of Air Separator

Fine powders have been accurately separated following Stokes' law into all or some of the fractions 0–2.5, 2.5–5, 5–10, 10–20, 20–40, and 40–100 microns.

For separation of the 0–2.5 micron fraction of a fine anhydrite powder (density 3.0), a 60.8-cm. separator tube and a 1-mm. inlet nozzle were used. At the required flow of 8.6 liters per minute there was a back pressure of 40 cm. of mercury. The initial rate of separation was 5.5 grams per hour, and the collected particles were less than 1 micron in size. Subsequently, as is true in general, the collected particle sizes approached the upper limit of the fraction. The end rate was constant at about 3 grams per hour and corresponded to attrition of the powder charge by the high-velocity air jet, the product consisting of 0–2.5 micron particles. As already observed, a suitable fine jet is necessary at particle sizes at and below 5 microns in order to disperse the clusters of electrostatically charged particles.

The same 60.8-cm. tube, but with a 2-mm. instead of a 1-mm. inlet nozzle, was employed in effecting the 2.5–5 micron separation of the same powder. The rate of air flow was now four times that in the 0–2.5 micron separation. Correspondingly, the initial rate of separation was higher, 30 grams per hour; after a few hours there was a constant attrition rate of 17 grams per hour, the collected particles ranging from 0 to 5 microns in size. As in the 0–2.5 micron separation, the attrition products presented a markedly different physical aspect from the average product, appearing gritty instead of fluffed up.

At a 0–5 micron separation of a Portland cement powder under conditions similar to the 2.5–5 micron separation of anhydrite, the initial rate of separation was the same, but the end rate approached zero and the collected particles were largely of the order of 5 microns in size. Thus there was practically no attrition of the cement powder. This difference in result with the cement powder as against the anhydrite, which is true in general, is due to the greater hardness of the former, 4 to 5 as against 3 to 3.5.

Separations at 10 microns of the 5–10 micron fraction were made with both the 30.4- and the 60.8-cm. tube, the optimum nozzle sizes being about 7 mm. and 14 mm., respectively. In the former case the initial rate of separation, at an air flow of 35 liters per minute, was 35 grams per hour; with the larger tube, necessitating an air flow of 140 liters per minute, the initial rate of separation was correspondingly about four times as great, 135 grams per hour. The 10-micron and subsequent separations were terminated at an end rate of about 3 grams per hour as a matter of convenience, owing to the slow approach to a zero rate and to the fact that, indicating the complete absence of attrition, the particle sizes were almost wholly in the upper boundary of the delimited fractions.

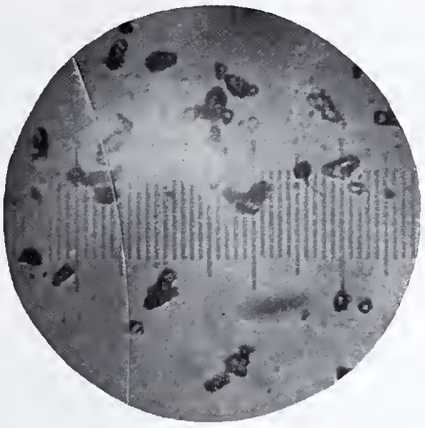
The 10–20 and 20–40 micron separations were made with a 15.2- and 7.6-cm. tube, respectively, with a nozzle size, as for the 5–10 micron fraction of 7 mm.; also, at an air flow four times as great, with a 30.4- and a 15.2-cm. tube, respectively, with a nozzle size of 14 mm. The initial rates of separation of these fractions were approximately the same as that of the 5–10 micron fraction at the same rate of air flow.

Collection of Powder Fractions

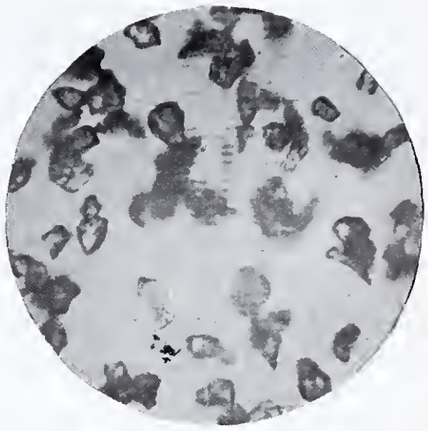
Filtering was adopted as the most convenient means of removing the separated fractions from the air stream. Closely woven cloth and canvas were tried but were found unsuitable because of the high loss of powder through the comparatively large pores.

A so-called white piano felt was quite satisfactory, except for a tendency to shed hairs, for collecting the finest fractions. As the quantity of powder fraction accumulated, the resistance to the air flow increased rapidly. To avoid frequent removal of the collected powder in order to relieve the back pressure, a large bag was required. A capacity of about 50

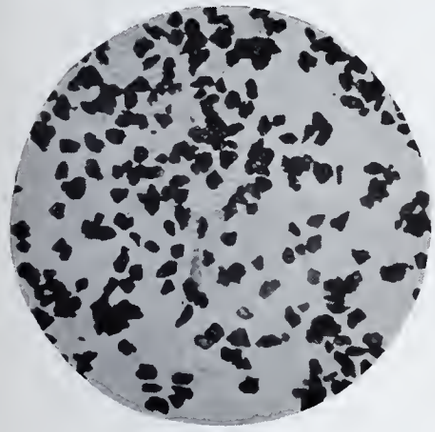
0–5 Microns, 310 ×



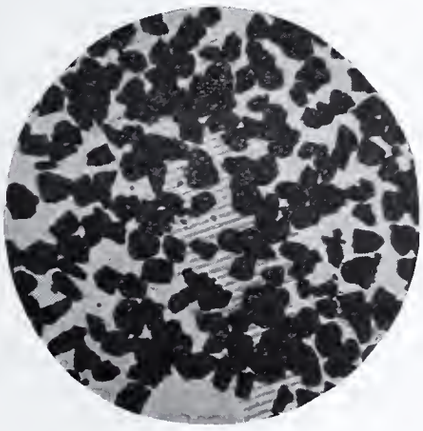
5–10 Microns, 310 ×



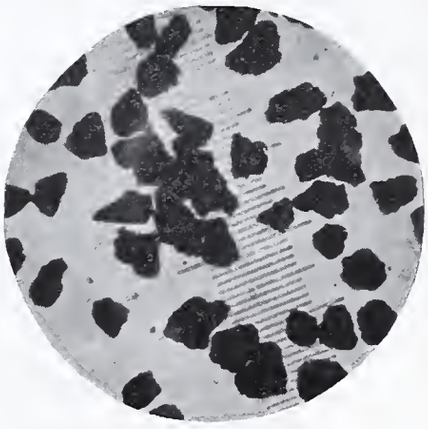
10–20 Microns, 310 ×



20–40 Microns, 70 ×



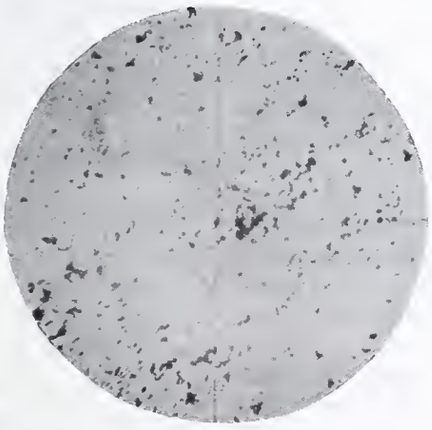
40–60 Microns, 70 ×



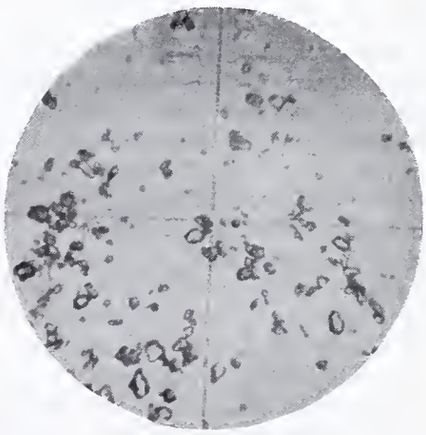
60–100 Microns, 70 ×

Figure 4—Portland Cement

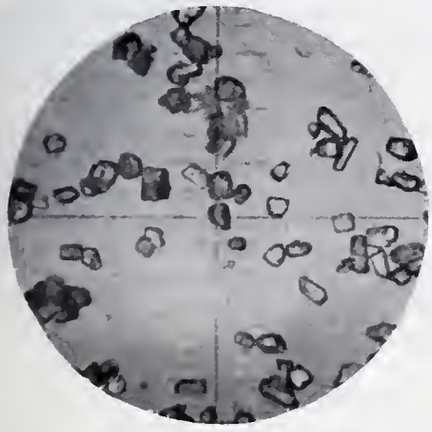
0–2.5 Microns, 190 ×



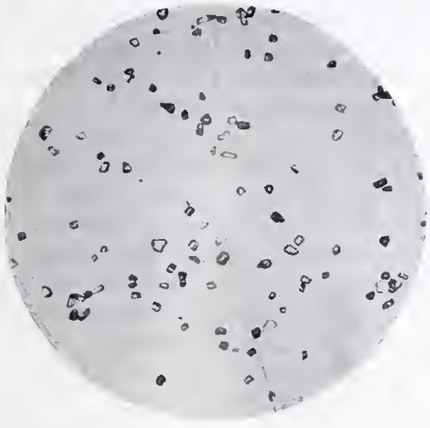
2.5–5 Microns, 190 ×



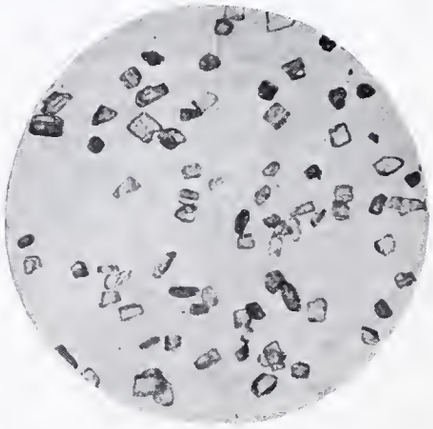
5–10 Microns, 190 ×



10–20 Microns, 190 ×



20–40 Microns, 45 ×



40–100 Microns, 45 ×

Figure 5—Anhydrite

liters was found suitable. The bag was conveniently wired to the rim of the circular top of a commercial tin funnel which was soldered at the other end to the exit gooseneck of the separator tube (Figure 3). By cutting the end of the bag and closing with a removable clip, a convenient outlet for the collected fractions is provided.

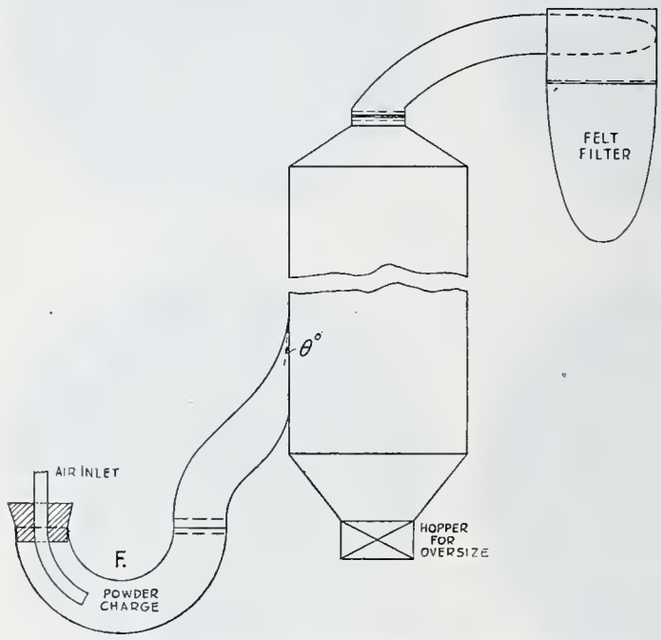


Figure 6—Assembly for Continuous Separation

As shown by tests made with this material, a paper extraction thimble, could it be had of sufficiently large capacity, would also be satisfactory for collecting the powder fractions.

Continuous Separation

Where large quantities of a powder are to be separated at a given particle size, continuous separation is evidently desirable. A suitable arrangement for effecting continuous separation with the apparatus described above is shown in Figure 6. A 7.6-cm. sheet-metal pipe connects the 7.6-cm. U-shaped powder container with an offset separator tube. The separated fraction passes up with the air to a bag filter, while the oversize falls into a hopper at the bottom of the separator. Continuous feed, though not employed in these experiments, could be maintained by means of a flexible connection at point *F* of the container.

Depending on the length of the 7.6-cm. connector tube and the angle Θ at which it entered the separator tube, the time required to blow out the major portion of a 1-kg. charge varied considerably. Although the time required was increased thereby, it was found that the most efficient recovery of fine product was secured when the angle Θ was nil—i. e., when the connecting tube entered directly upwards into the separator tube. Consequently, this arrangement was used in the separations described below.

With a 38.1-cm. separator tube, an inlet nozzle 25 mm. in diameter, and an air flow of 500 liters per minute, corresponding to separation at a particle size of 30 microns, 905 grams of a 1-kg. charge of Portland cement powder were blown out of the container in 10 minutes; in other words, a rate of feed could be maintained of 5.4 kg. per hour. The separated fraction was analyzed (*2*) and microscopically examined. It was found to consist entirely of particles below 30 microns. The oversize, however, was badly contaminated with particles in the range 0 to 30 microns, indicating that only a fraction of this material in the original powder had been separated.

The latter was analyzed (*2*) and found to contain 54.8 per cent by weight in the range 0 to 30 microns. Four separations were made on the successive residues from 1 kg. of powder with results as shown in Table II.

Table II—Continuous Separation at 30 Microns of 1 kg. of Cement Powder

Number	Amount Separated	0–30 Micron Material Separated	
		Residual	Original
	Grams	%	%
1	155	28.3	28.3
2	100	25.4	18.2
3	63	21.5	11.5
4	40	17.4	7.3

It is seen from column 3 of Table II that the efficiency of the successive separations based on the actual 0–30 micron content of the residues decreases with each successive separation. From column 4 it is seen that the first separation nets 28.3 per cent of the total 0–30 micron material in the powder; in successive separations the figure decreases until it is only 7.3 per cent for the fourth separation. In a total of four separations, 65.3 per cent of the original 0–30 micron material has been recovered from the powder. This result is perhaps to be expected in view of the large surface exposed to fines in the above 30-micron oversize in the cement powder.

Since 155 grams of 0–30 micron powder were collected in 10 minutes, it follows that the rate of recovery during the first cut is 0.93 kg. per hour. In what may be called the batch separation with set-up as in Figure 3, but otherwise under the same conditions of air flow and nozzle size, but with a 30.4-cm. separator tube, the initial rate was 0.73 kg. per hour. Consequently, it may be concluded that the rate of recovery of fine fraction is greater in the arrangement for continuous separation than in the batch process.

In another experiment on continuous separation of Portland cement powder, the conditions were the same as before but the inlet nozzle was much finer, 9 mm. instead of 25 mm. Eight hundred grams of powder were blown out in 11 minutes, or the equivalent rate of feed was 4.4 kg. per hour. This is only about 0.8 of the rate with the larger inlet nozzle. The efficiency was also lower, as will be seen from Table III, which is constructed in the same way as Table II.

Table III—Continuous Separation at 30 Microns of 1 kg. of Cement Powder

Number	Amount Separated	0–30 Micron Material Separated	
		Residual	Original
	Grams	%	%
1	110	20.0	20.0
2	75	17.1	13.7
3	51	14.0	9.3
4	29	9.3	5.3

From column 3 of Table III it is seen that, as before, the efficiency decreases with each successive separation. The maximum efficiency is 20.0 per cent as against 28.3 per cent with the larger inlet nozzle. Since 110 grams were separated in 11 minutes, the rate of recovery of fine product is 0.60 kg. per hour compared to 0.93 kg. per hour with the larger inlet nozzle.

In contrast to the above result with a fine nozzle, tests with a 30-mm. inlet indicated a slightly higher rate of separation and efficiency of recovery. In accordance with previous conclusions on the optimum ratio of air flow to nozzle size, an inlet approaching this diameter would seem most suitable at the air flow in question, 500 liters per minute.

Acknowledgment is made of the coöperation of C. M. Davis, mechanic, in the required constructions.

Literature Cited

(1) Millikan, *Ann. Physik*, **41**, 763 (1913).
(2) Roller, U. S. Bur. Mines, *Tech. Paper* **490** (1930).

Electroanalytical Separations in Ammoniacal Fluoride Solutions

I—Separation of Copper from Arsenic and Antimony[1]

N. Howell Furman

Frick Chemical Laboratory, Princeton University, Princeton, N. J.

A new procedure has been described for the electrolytic separation of copper from arsenic and antimony in ammoniacal fluoride solution.

Some qualitative observations have been made upon the rapidity of the oxidation of trivalent antimony by persulfate under various conditions.

THIS study originated from a consideration of the problem of electrolytic deposits of copper contaminated with arsenic and antimony. It was shown in preliminary experiments that a known weight of copper could be coated electrolytically with arsenic and antimony, and the deposit could then be dissolved in a mixture of nitric and hydrofluoric acids, after which the procedure described in this paper gave correct results for the copper.

Ammoniacal solutions of quinquevalent arsenic or antimony may, as is well known, be electrolyzed with currents as great as 5 to 10 amperes per square decimeter of cathode surface, without deposition of arsenic or antimony at the cathode. This fact has been made the basis of the separation of a number of metals from arsenic and antimony, for example, cadmium (*13*), copper (*7*), nickel (*5*), or silver (*14*) from arsenic, or cadmium (*15*), copper (*11*, *16*) or silver (*3*) from antimony.

Methods which have been developed previously offer no simple scheme for the solution and complete oxidation of arsenic and antimony when admixed with copper. Bosek (*1*) has shown conclusively that the complete oxidation of antimony with nitric acid is a matter of very considerable difficulty.

A mixture of copper, arsenic, and antimony, whether derived by electrolytic deposition or otherwise, may be dissolved in a mixture of nitric and hydrofluoric acids (*9*). The oxidation of the last traces of trivalent arsenic and antimony in such a solution may be effected very readily with potassium persulfate. This method has been studied by McCay in connection with an investigation of the separation of arsenic from antimony (*9*). He found that some 20 to 30 minutes of boiling of the acid solution with an excess of persulfate would complete the oxidation of arsenic and the antimony. The author has found that the oxidation goes very rapidly in faintly acid solution; 2 to 3 minutes' boiling then suffices to complete the oxidation.

Experimental Procedure

The materials used in the separations were of known purity, being part of a large stock that had been tested in previous investigations (*4*, *10*). In connection with these previous studies it was shown that antimony is not reduced during the electrolysis of an ammoniacal fluoride solution of potassium antimoniate.

Nitric acid solutions of pure electrolytic copper were prepared and the metal was determined by electrodeposition. Table I gives the results.

Table I—Determination of Copper in Nitric Acid Solutions

Nitric Acid Soln.	Copper Found	
	Soln. I	Soln. II
Cc.	*Gram*	*Gram*
25	0.2047	0.1991
25	0.2044	0.1994
50	0.4086	0.3983
25	0.2044	....
25	Av. 0.2044	0.1992

[1] Received March 4, 1931.

Weighed amounts of pure antimony and of arsenious oxide were dissolved in 3 to 5 cc. of 48 per cent hydrofluoric acid and 25 cc. of nitric acid (1 volume of acid of sp. gr. 1.42 and 4 volumes of water). A measured volume of standard copper solution was added. Oxidation of arsenic and antimony was completed by adding a moderate excess of potassium persulfate (1 to 2 grams). A few of the oxidations were completed by boiling the strongly acid solution for 30 minutes. Subsequent oxidations were effected by boiling the acid solution 2 to 3 minutes, followed by immediate neutralizations with ammonia. The efficiency of this procedure was established by numerous qualitative tests of which the following is typical: A solution containing 0.12 gram of trivalent antimony, 1.25 cc. of 48 per cent hydrofluoric acid, 1.25 cc. of concentrated sulfuric acid, and 1 gram of potassium persulfate in 35 cc., gave a distinct qualitative test for trivalent antimony after several minutes' boiling. In one instance a positive test was obtained after boiling for 20 minutes, and a further test after 25 minutes showed the oxidation to be complete. A similar solution, previously neutralized with ammonia, then cleared by adding the minimum amount of 6 *N* nitric acid, was boiled 3 minutes after adding 1 gram of the persulfate; the oxidation was then found to be complete. The qualitative tests were made by the Rose method (*2*), and by treating the solution with hydrogen sulfide, which under these conditions gives no immediate coloration or precipitate unless trivalent antimony is present.

Table II—Separation of Copper from Arsenic and Antimony

Detn.	Antimony Present	Arsenic Present	Copper Present	Copper Found[a]	Error
	Gram	*Gram*	*Gram*	*Gram*	*Mg.*
1	0.1805	....	0.2044	0.2042	−0.2
2	0.4070	....	0.2044	0.2043	−0.1
3	0.3530	....	0.2044	0.2047	+0.3
4	0.2970	....	0.1992	0.1997	+0.5
5	0.1170	0.0758	0.1992	0.1985	−0.7
6	0.2110	0.0987	0.1992	0.1993	+0.1
7	0.1972	0.1485	0.3984	0.3977	−0.7
8	0.1058	0.1582	0.3984	0.3986	+0.2

[a] Values corrected for small amounts of platinum dissolved from anode and deposited at cathode with the copper. In determinations 5 to 8 a hard anode (platinum-iridium) was used and no weighable amount of platinum appeared in copper deposit. In the other cases from 0.2 to 0.7 mg. was found when copper was dissolved in nitric acid. Proof of presence of platinum was obtained by formation of potassium chlorplatinate, or by stannous chloride reduction test.

Copper was separated from the cold, strongly ammoniacal solution by electrolysis after the completion of the oxidation. The total volume was 100 cc., containing 5 to 10 cc. of ammonia of sp. gr. 0.90. The series of separations recorded in Table II was made with stationary electrodes; current density 0.1 to 0.3 amperes per square decimeter and 2 to 4 volts applied at the electrodes. The solution was in a paraffined beaker, and covered with paraffined split cover glasses. Complete deposition occurred in 5 to 8 hours. A number of electrolyses were allowed to continue overnight (15 to 18 hours) as a matter of convenience.

The copper deposits were carefully tested qualitatively for presence of antimony and arsenic. The tests were generally

negative. In one case the residue obtained upon acidifying the sulfosalt filtrate with acetic acid, after removal of the copper sulfide, gave a coloration with hydrogen sulfide like that due to antimony; the color was not as intense as that produced by 0.01 mg. of antimony under similar conditions.

A series of rapid separations was made using current densities of 4 to 8 amperes per square decimeter of cathode at a voltage of 8 to 12. The anode (a platinum-blade stirrer) was rotated at 500 to 700 r. p. m. The copper was deposited completely in 35 to 45 minutes. The results are shown in Table III.

Table III—Rapid Separation of Copper from Arsenic and Antimony

Detn.	Antimony Present	Arsenic Present	Copper Present	Copper Found[a]	Error
	Gram	*Gram*	*Gram*	*Gram*	*Mg.*
1	0.2342	....	0.1992	0.1997	+0.5
2	0.2021	....	0.3984	0.3977	−0.7
3	0.1733	0.2094	0.1992	0.1987	−0.5
4	0.1028	0.1493	0.1992	0.1998	+0.6
5	0.1082	0.1511	0.3984	0.3981	−0.3

[a] Corrected for platinum (*cf.* note, Table II); amounts found 0.2 to 0.7 mg.

In a subsequent series of determinations, shown in Table IV, both copper and antimony were determined. After the copper had been deposited, the nitrates and fluorides were expelled by evaporation with an excess of sulfuric acid. McCay (*9*) has shown that this operation may be done in a quartz dish when the antimony is to be determined volumetrically. The reduction was effected by heating with about 1 gram of roll sulfur at about the temperature of boiling sulfuric acid (*8*), for 30 minutes. The antimony was then determined by titration with 0.05 *N* potassium permanganate solution which had been standardized against pure dry sodium oxalate (*6*).

Table IV—Determination of Both Copper and Antimony

Copper		Antimony	
Present	Found	Present	Found
Gram	*Gram*	*Gram*	*Gram*
0.1992	0.1989	0.1211	0.1209
0.3984	0.3986	0.0926	0.0931
0.3984	0.3989	0.1536	0.1531
0.1992	0.1991	0.0880	0.0874

Literature Cited

(1) Bosek, *J. Chem. Soc.*, **67**, 515 (1895).
(2) Fresenius, "Qualitative Analysis," translated by Mitchell, p. 362, Wiley, 1921.
(3) Freudenberg, *Z. physik. Chem.*, **12**, 109 (1893).
(4) Furman, *J. Am. Chem. Soc.*, **40**, 895 (1918).
(5) Furman, *Ibid.*, **42**, 1789 (1920).
(6) McBride, *Ibid.*, **34**, 393 (1912).
(7) McCay, *Chem.-Ztg.*, **14**, 509 (1890).
(8) McCay, *J. Am. Chem. Soc.*, **32**, 1241 (1910); **36**, 2380 (1914).
(9) McCay, *Ibid.*, **36**, 2375 (1914).
(10) McCay and Furman, *Ibid.*, **38**, 640 (1916).
(11) Puschin and Trechinsky, *Chem.-Ztg.*, **28**, 482 (1904).
(12) Rose, *Pogg. Ann.*, **3**, 441 (1924).
(13) Schmucker, *J. Am. Chem. Soc.*, **15**, 195 (1893); *Z. anorg. Chem.*, **5**, 199 (1894).
(14) Smith and Frankel, *Am. Chem. J.*, **12**, 428 (1890).
(15) Smith and Wallace, *Z. anorg. Chem.*, **4**, 273 (1893).
(16) Smith and Wallace, *J. Am. Chem Soc.*, **15**, 32 (1893).

Graphical Tensile-Testing Machine for Rubber Threads[1]

S. H. Hahn and E. O. Dieterich

B. F. Goodrich Co., Akron, Ohio

Among the many types of physical testing equipment which have been designed for or applied to the needs of the rubber industry, there has never appeared an entirely satisfactory graphical machine for performing tensile tests on small rubber samples, such as the threads and tapes used in making golf balls and elastic fabrics and cords. None of the common machines can be applied directly to the testing of single threads, and even tests on pieces of dumbbell shape are quite unsatisfactory, largely because the standard machines are comparatively insensitive at low elongations and tensions and also because they depend on the personal accuracy of an operator to observe several points along the stress-strain curve. The Schopper ring test is not entirely successful for tests on threads.

Accordingly it appeared that such tests on light rubber threads could best be made on a curve-drawing machine, designed and constructed especially for the purpose. In many cases, the use of any other machine would have been impossible because frequent tests had to be run on single, cut threads from factory production and on samples taken from storage or from woven fabric.

General Design Requirements

Several rather severe restrictions on the design were imposed by the nature of the samples to be tested. These are as follows:

(1) The breaking strength of the smallest threads to be tested is comparatively low. A 50 × 50 gage thread, the smallest ordinarily cut, has a cross-sectional area of only 0.00258 sq. cm. (0.0004 sq. in.) and a breaking strength of less than 450 grams (1 pound). At the same time the heavier threads require a maximum tensile force of about 2 kg. (4 pounds), so that a full scale range of 2.26 kg. (5 pounds) has to be provided.

(2) Elongations up to about 1000 per cent on a 5.08-cm. (2-inch) gage length have to be accommodated in testing pure gum stocks.

(3) A high degree of sensitivity as compared with the usual machine is required in the region of 200 to 700 per cent elongation where the tension usually varies from about 40 to 700 grams (0.1 to 1.5 pounds).

(4) Whatever the grips used, they must not allow the length under test to increase by creep or slippage of the rubber, and they must secure the thread so the gage marks are in full view.

It was found possible to achieve the result desired by modifying a small 11.32-kg. (25-pound) Scott machine designed for graphical stress-strain tests on tire cords. Friction was reduced to a minimum by the use of rotating bearings of small diameter instead of sliding parts, by the elimination of the thread-pulley-counterweight arrangement on the pen motion, by substituting wires for the usual roller chain supporting the upper pulling head of the machine, by using a lighter pen pressure, and by the elimination of the usual ratchet for catching the balance wheel at the breaking point of the sample. The full scale capacity of the machine was reduced to 2.26 kg. (5 pounds) with provision for doubling the range without change of intermediate scale divisions. At the same time, the chart length was not changed materially because a reducing motion provided a chart traverse only one-third that of the lower pulling head.

Tests and almost daily use during the past eighteen months

[1] Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

have shown the machine to be entirely satisfactory. Even with the pen in contact with a stationary chart the machine is sensitive to a change of force at the upper head of less than 2 grams (0.005 pound) at any part of its range, a sensitivity better than 0.1 per cent of the full range. The accuracy of a such a machine depends primarily on the care

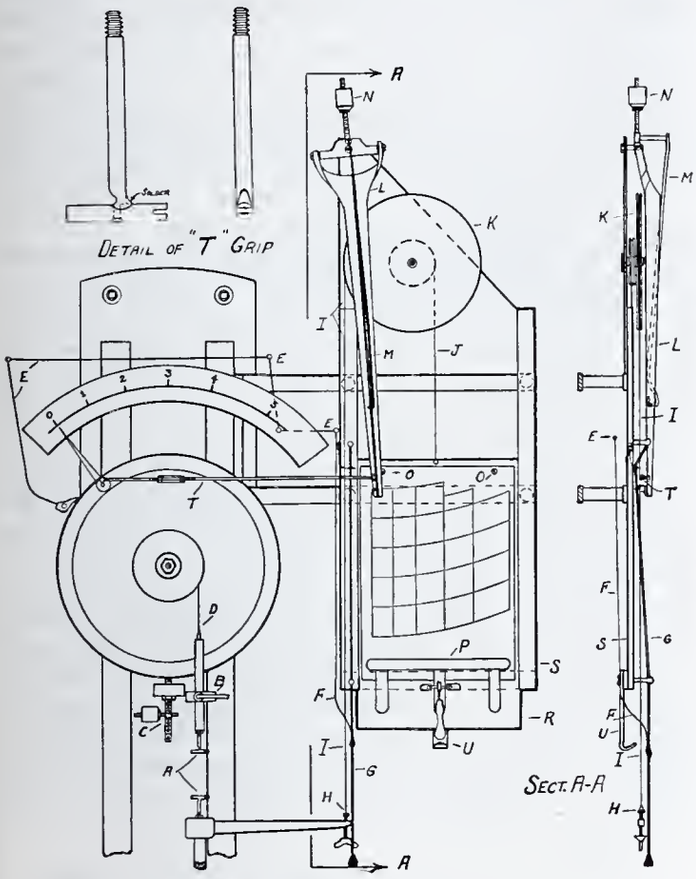


Figure 1—Graphical Rubber-Thread Tester, a Modified Scott Tensile Machine

with which the master chart is made and on the accuracy of the printed charts. Checks made on the machine now in use in the writers' laboratories, after several changes of range and recalibrations, showed the indications on the chart to be accurate to about 5 grams (0.01 pound) over the range 0 to 2 kg. (0 to 4 pounds).

Details of Design and Construction

The first problem of the new design shown in Figure 1 was the development of a satisfactory grip, since no amount of work on other parts of the machine would be of much use if the grips allowed the sample to creep or slip. No design was found entirely satisfactory, but it was found possible to secure the ends of the thread sample at the gage marks by use of a simple knot whereby the thread was snubbed under nearly its maximum elongation around a rod of small diameter This idea was applied in the form of notched tee of cold-rolled steel, 0.159 cm. ($^1/_{16}$ inch) in diameter (see detail of Figure 1), to which the operator secures the thread by stretching it for a short distance on either side of the gage mark, wrapping it around the rod with the mark over the center of the rod in the horizontal plane, crossing one or more times over the first turn immediately above the gage mark, and slipping the free end in the notch at one end of the tee. The appearance of the thread in place on the grip is shown in detail in Figure 2. The upper grip is held in a spring vise, *B*, while fastening the thread. The machine is arranged to return the lower head automatically to a position such that the center-to-center distance between grips is exactly 2 inches (5.08 cm.), the gage length used.

It was hoped that this new grip design would make possible testing up to the true breaking point of the rubber, but subsequent use has shown that most samples break at one grip or the other. A break at one of the grips always occurs at a lower stress than the maximum breaking strength of the sample, because such breaks are caused by minute chafe marks due to slight creeping of the rubber over the grip as the sample approaches its breaking elongation. The duplication of results, the shape and slope of the stress-strain curve up to about 700 per cent of elongation, and the stiffness or tensile force at a given elongation were, after all, more important than the ultimate breaking strength and elongation in the investigation for which this machine was required.

The pen is carried by a long arm of light-weight construction, *L*, which is counter-balanced by the weight, *N*, and operated by the light rigid metal link, *T*. The pen arm is hinged on an axis perpendicular to its pivot shaft so that the pen may be raised from the paper between tests. A wire of spring steel, *M*, is made a part of the pen-arm construction in such a way that it serves both as a spring to supply a light pen pressure and as a catch to hold the pen arm in the raised position. The wire is bent to slide in an L-shaped slot near the lower end of the arm. When the arm is raised the end of the wire springs into the short end of the L-slot and holds the arm in that position until it is released by the operator. A vertical, flexible cord is supported behind the pen-arm link in such a way that a light jerk on the cord will move the link forward and raise the pen so that the catch may operate.

The same cord also serves to operate the ratchet device which is used to catch the machine's balance wheel at the instant of rupture of the thread under test. The ratchet spring is so light that the unbalanced weight of the wheel holds the ratchet dog in place until the wheel is advanced slightly, whereupon the wheel may be returned by hand to its zero position. This device was found necessary to prevent the rapid return and violent rebound of the balance wheel which would otherwise occur after failure of the test sample.

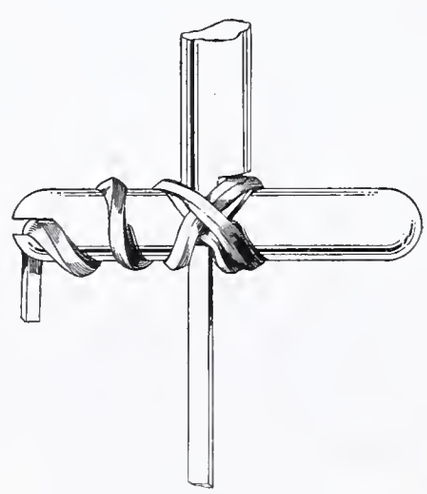


Figure 2—Method of Mounting Thread Test Pieces on Upper Grips

The connecting link, *T*, was made light enough to have very little effect on the position of the comparatively heavy balance wheel so that the same scale graduations may be used for any tensile range greater than 5 pounds (2.26 kg.).

The chart coördinates are vertical straight lines for the elongation scale, and parallel curves which are concave upwards and slope upwards from left to right for the tensile scale. The vertical scale is made one-third as long as the

maximum travel of the lower head of the machine by virtue of the 1:3 reducing-wheel motion by which the motion of the lower head is transmitted to it. The curved coördinates were laid out from a drawing of a "zero extension" curve to the full tensile capacity of the machine, using a rigid connection between upper and lower heads.

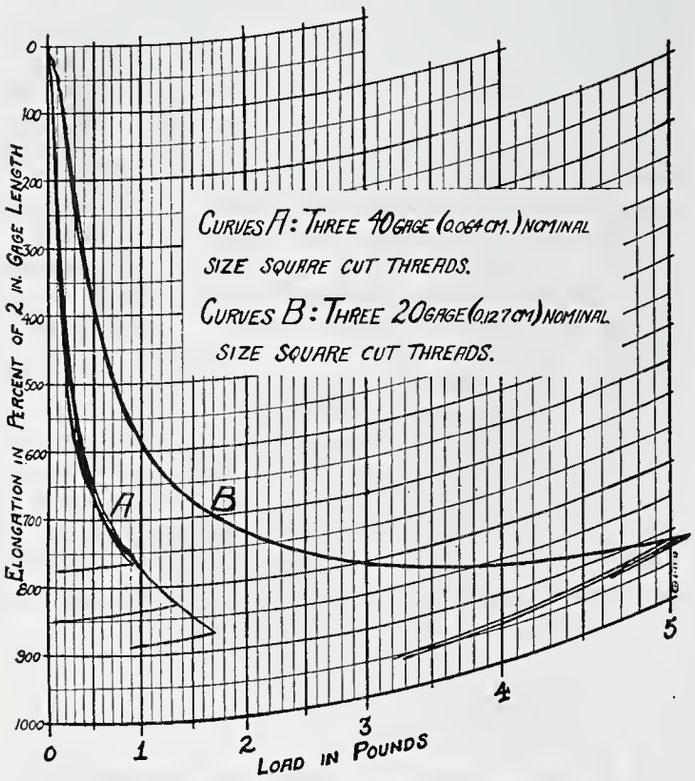


Figure 3—Graph Drawn by Modified Machine

The chart carriage is a rectangular machined plate of 0.318-cm. (1/8-inch) steel supported from the smaller pulley by a fine music wire. A similar wire connects the arm carried by the lower head and the groove in the large pulley. The carriage is guided by accurately machined steel guides supported on a framework bolted to the main frame of the testing machine. A small spring steel clip, *U*, placed at the bottom of the guides, prevents the carriage from dropping out in the event of breakage of either wire.

Friction in the force-measuring balance wheel was reduced to a minimum by substitution of a bifilar suspension of fine music wire for the usual small roller chain which was found to be the source of a small variable friction.

The tensile capacity of the machine, although usually fixed at 2.26 kg. (5 pounds), may be increased to 4.52 kg. (10 pounds) or any suitable larger amount by the addition of small weights on the threaded rod, *C*. Calibration is effected by adjustments of both sets of weights, the combination of weights adjustable at right angles to each other in the plane of the wheel with small adjustments of the indicator-needle angle, length of connecting links, and pen radius, being sufficient to bring the device to its original calibration in case of derangement of the original settings.

No change was made in the balance wheel, other than the reduction of the amount of unbalance. A wheel or lever of much lighter construction could readily be substituted for the heavy cast wheel which is standard on the Scott machine, if a reduction of inertia in the measuring system were sought. However, a careful calculation has shown that no serious effects from this source exist when testing threads at the ordinary pulling speeds of 25.4 or 50.8 cm. (10 or 20 inches) a minute.

The extension range of the machine was increased to give a travel of about 50 cm. (20 inches) by lowering the gear box as far as possible. The movement of the upper head of the machine causes the elongation capacity to be less at higher tensiles than it is at zero force.

Operation of Machine

In using the machine the operator locks the upper grip in a position such that the reading on the tensile scale is zero. The printed chart is then secured to the carriage by slipping its perforations over pins, *O*, one of which is adjustable, and fastening it under the clamp bar, *P*. The chart is adjusted so that its vertical coördinates parallel the guide bars and so that its zero force line will coincide with the zero position of the pen. The zero vertical position of the chart is adjusted by use of the adjustable anchor screw, *H*, to which the wire from the lower head of the machine is fastened.

With the upper head still clamped, the operator fastens the previously marked gage length of thread to the two grips. In installing the sample the operator stretches a small portion of the sample near the gage mark to somewhat less than the breaking elongation of the rubber as judged by the feel, lays the gage mark so that it will be horizontally over the center of the cross rod of the tee, and wraps it around the rod and upon itself in a figure eight fashion for four or more turns, always being careful that the turns cross each other slightly above the lower edge of the gage mark so as to leave the center of the gage mark in full view. The loose end of the thread is secured in the narrow slot at the end. Since the machine is arranged to stop the lower grip in the correct starting position, the installation of the correct gage length over the centers of the grips assures starting the test with zero tensile force on the rubber. The clamp is released by pulling the movable jaw outward and turning it through 90 degrees. The pen is then lowered to the paper by pressing the end of the spring wire out of the short end of the L-slot in the pen arm.

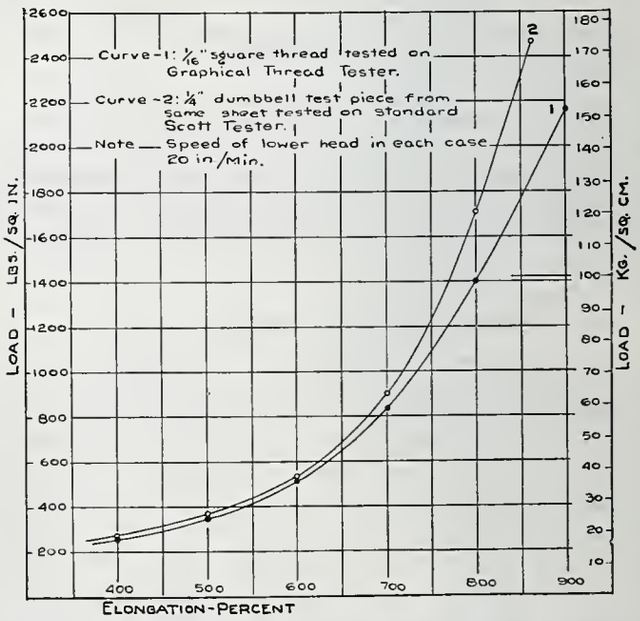


Figure 4—Comparison of Tests on Standard Dumb-Bell-Shaped and Square-Cut Thread Samples

The lower head is then set in motion in the usual way and the stress-strain curve is drawn automatically. At break, a jerk on the cord, *G*, releases the pen from the paper and catches the balance wheel near its maximum deflection. The wheel may then be returned under control to its zero position by the operator.

Illustrations of the performance of the modified machine are given in Figure 3, which is a photograph of a graph drawn by the machine. These curves demonstrate that slippage at

the grips has been entirely overcome, otherwise there would be a larger spread between the individual curves for the test pieces from a given sample. Of course, variations in the cross section of the test pieces will prevent coincidence of the separate stress-strain curves, but when the proper corrections have been made, the calculated points show close agreement.

Figure 4 is a comparison of the curves obtained for single threads using this machine, and for dumb-bell-shaped test pieces cut from the same sheet and tested in the regular fashion with the Scott rubber tester. On account of the great differences in geometrical configuration of the two types of test pieces and in the rate of loading, it is to be expected that there will be appreciable differences in the stress-strain curves, such as are indicated here in the region of higher elongations.

Recommended Specifications for Analytical Reagent Chemicals[1]

Perchloric Acid 60 Per Cent, Cadmium Chloride ($CdCl_2.2^1/_2H_2O$), Chromium Trioxide, Lead Chromate, Lead Nitrate, Magnesium Oxide, Mercuric Chloride, Mercurous Chloride, Sodium Nitroferricyanide, Uranium Nitrate

W. D. Collins, Gregory P. Baxter, H. V. Farr, J. V. Freeman, Joseph Rosin, G. C. Spencer, and Edward Wichers

Committee on Analytical Reagents, American Chemical Society

THE specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (*1, 2, 3, 4, 5, 6, 7*) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (*3*). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

Acid, Perchloric—60 Per Cent

Requirements

Assay—Not less than 59 per cent $HClO_4$.
Non-Volatile Matter—Not more than 0.015 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Nitrogen Compounds (as N)—Not more than 0.004 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Ammonia (NH_3)—Not more than 0.001 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—Not more than 0.0002 per cent.

Tests

Assay—Titrate a weighed portion of the acid, after suitable dilution, with standard alkali hydroxide solution, using phenolphthalein as indicator.

Non-Volatile Matter—Evaporate 9 cc. of the acid and ignite gently. The residue should not weigh more than 0.0015 gram.

Chloride—Dilute 5 cc. with 40 cc. of water, add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.05 mg. of chloride ion in the same volume of a solution containing the quantities of nitric acid and silver nitrate used in the test.

Nitrogen Compounds—Dilute 1 cc. of the sample in a flask with 10 cc. of ammonia-free water, add 10 cc. of 10 per cent sodium hydroxide solution and about 0.5 gram of aluminum wire in small pieces, and allow to stand for 3 hours protected from loss or absorption of ammonia. Dilute to 50 cc., decant from any insoluble matter, and add 2 cc. of Nessler's reagent. The color should not be greater than is produced by 0.04 mg. of N as NH_3 in the same volume of a solution containing the quantities of sodium hydroxide and Nessler's reagent used in the test.

Sulfate—Dilute 10 cc. of the acid with 35 cc. of water and neutralize with ammonium hydroxide, using litmus paper as indicator. Add 0.5 cc. of dilute hydrochloric acid (1 part strong acid in 10) and 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Any precipitate of barium sulfate should not weigh more than 0.0012 gram. Correction should be made for the weight obtained on running a blank, including filtration, using the quantities of reagents used in the test. Most of the ammonia should be removed by evaporation so that only a small quantity of acid will be required for neutralization before acidifying for the precipitation.

Ammonia—Dilute 2 cc. of the sample with 40 cc. of ammonia-free water, add 10 cc. of 10 per cent sodium hydroxide solution and 2 cc. of Nessler's reagent. Any yellow color produced should not be greater than is given by 0.02 mg. of NH_3 in the same volume of a solution containing the quantities of sodium hydroxide and Nessler's reagent used in the test.

Heavy Metals, Iron—Dilute 5 cc. with 40 cc. of water, add 5 cc. of hydrogen sulfide water, and make alkaline with ammonium hydroxide. No brown color should be observed. Any greenish color should not be greater than is produced by 0.01 mg. of iron in an equal volume of alkaline sulfide solution.

Cadmium Chloride ($CdCl_2.2^1/_2H_2O$)

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Nitrate (NO_3)—To pass test (limit about 0.003 per cent).
Sulfate (SO_4)—Not more than 0.005 per cent.
Ammonia (NH_3)—Not more than 0.005 per cent.
Copper (Cu)—To pass test (limit about 0.0005 per cent).
Iron (Fe)—To pass test (limit about 0.001 per cent).
Lead (Pb)—To pass test (limit about 0.005 per cent).
Substances Not Precipitated by Ammonium Sulfide—Not more than 0.2 per cent.
Zinc (Zn)—To pass test (limit about 0.05 per cent).

Tests

Insoluble Matter—Dissolve 10 grams in 50 cc. of hot water and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the insoluble residue should not exceed 0.0005 gram.

Nitrate—To a solution of 2 grams in 10 cc. of water add 10 cc. of sulfuric acid and 2 drops of indigo solution (1 in 1000). The blue color should not disappear in 10 minutes.

Sulfate—Heat to boiling the filtrate and washings obtained in the test for insoluble matter (which should measure not more than about 150 cc.), add 1 cc. of 1 *N* hydrochloric acid and 5 cc. of 10 per cent barium chloride solution and allow to stand overnight. Filter, wash thoroughly, and ignite. The weight of the barium sulfate should not be more than 0.0012 gram.

[1] Received March 6, 1931. Presented in connection with the report of the Committee on Analytical Reagents at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Correction must be made for a blank test made with the same quantities of reagents and including the filtration and ignition of the paper.

Ammonia—Dissolve 2 grams in 75 cc. of water and add with stirring 25 cc. of a cold 10 per cent solution of sodium hydroxide. After allowing the precipitate to subside, decant 50 cc. of the clear liquid and add 2 cc. of Nessler's solution. Any coloration produced should not be greater than is produced by 0.05 mg. of NH_3 under the same conditions.

Copper and Iron—Dissolve 1 gram in 20 cc. of water, add 2 drops of nitric acid, bring to a boil, and allow to cool. Add 2 drops of a 10 per cent solution of potassium ferrocyanide and stir well. The precipitate formed should not have a red or blue tint after standing 15 minutes.

Lead—Dissolve 1 gram in 25 cc. of water, add 5 drops of glacial acetic acid, and filter if necessary. Add 1 cc. of 1 per cent potassium chromate solution. Any turbidity or precipitate should not be greater than is produced by 0.05 mg. of lead under the same conditions.

Substances Not Precipitated by Ammonium Sulfide—Dissolve 2 grams in 150 cc. of water, add ammonium hydroxide to dissolve the precipitate first formed, and pass hydrogen sulfide gas through the solution to precipitate all the cadmium. Filter off 75 cc. of the clear liquid, add 5 drops of sulfuric acid, evaporate to dryness, and ignite gently. The weight of the ignited residue should not be more than 0.0020 gram.

Zinc—Dissolve 0.2 gram in 100 cc. of water and add 3.5 cc. of sulfuric acid. Heat to boiling and pass a rapid stream of hydrogen sulfide for 15 minutes, allowing the solution to cool during the passage of the gas. Filter at once, evaporate the filtrate and expel practically all of the sulfuric acid. Take up the residue with 5 cc. of water and add ammonium hydroxide until the solution is just alkaline to litmus paper. Then make it just acid to the litmus paper with 0.1 *N* sulfuric acid. Dilute to 100 cc. and pass a rapid stream of hydrogen sulfide for 5 minutes. No white precipitate or turbidity should be produced.

Chromium Trioxide

Requirements

Assay—Not less than 96 per cent.
Insoluble Matter—Not more than 0.010 per cent.
Chloride (Cl)—To pass test (limit about 0.005 per cent).
Sulfate (SO_4)—Not more than 0.005 per cent.
Alkali Salts—Not more than 0.2 per cent.
Iron, Aluminum, Barium, Etc.—Not more than 0.03 per cent.

Tests

Assay—Dissolve 5 grams in water, make up to 1000 cc. and mix well. Transfer 25 cc. of the solution to a glass-stoppered bottle and dilute with 100 cc. of water. Add 5 cc. of hydrochloric acid and 3 grams of potassium iodide and allow to stand in the dark for 15 minutes. Dilute with another 100 cc. of water and titrate the liberated iodine with 0.1 *N* sodium thiosulfate solution, adding a little starch towards the end. Correct for the thiosulfate consumed in a blank test made with the same quantities of reagents.

Insoluble Matter—Dissolve 10 grams in 100 cc. of water, and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the insoluble residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water, add 10 cc. of nitric acid, heat to about 50° C., and add a few drops of 0.1 *N* silver nitrate solution. No turbidity should be produced in 5 minutes.

Sulfate—Dissolve 10 grams in 350 cc. of water and add 5 grams of sodium carbonate. Heat to boiling and add 35 cc. of a solution containing 1 gram of barium chloride and 2 cc. of hydrochloric acid per 100 cc. of solution. Digest on the steam bath for 2 hours and allow to stand at room temperature overnight. If any precipitate forms, filter, wash, and ignite it. Fuse the residue with 1 gram of sodium carbonate. Extract the fused mass with water and filter off the insoluble residue. Add 5 cc. of hydrochloric acid to the filtrate, dilute to about 200 cc., heat to boiling, and add 10 cc. of alcohol. Digest on the steam bath until reduction of chromate is complete as indicated by the change to a clear green or colorless solution. Neutralize the solution with ammonium hydroxide and add 2 cc. of hydrochloric acid. Heat to boiling and add 10 cc. of a 10 per cent solution of barium chloride. Digest on the steam bath for 2 hours and allow to stand overnight. Filter, ignite, and weigh. Correction must be made for a blank determination on the reagents, including filtration and ignition of the filter paper.

Alkali Salts—Carefully ignite 0.5 gram in a porcelain dish until decomposed. Cool thoroughly, triturate well the residue with 10 cc. of hot water, filter through a small filter paper, and wash with about 25 cc. of hot water. Evaporate the filtrate and washings to dryness in a small porcelain dish, and ignite. Warm the residue with 10 cc. of water, filter, and wash with small quantities of hot water until the washings are colorless. Evaporate the filtrate and washings to dryness, ignite gently, and weigh. The weight of the residue should not exceed 0.0010 gram.

Iron, Aluminum, Barium, Etc.—Dissolve 5 grams in 100 cc. of water, heat, add 10 cc. of ammonium hydroxide, and boil for 5 minutes. Filter, dissolve the precipitate in warm dilute hydrochloric acid (1 + 1), wash, and dilute to 20 cc. Make the solution barely alkaline with sodium peroxide, boil for 5 minutes, acidify with dilute sulfuric acid, add a slight excess of ammonium hydroxide, boil for 5 minutes, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not exceed 0.0015 gram.

Lead Chromate

Requirements

Assay—Not less than 98 per cent $PbCrO_4$.
Soluble Matter—Not more than 0.20 per cent.
Carbon Compounds (as C)—Not more than 0.003 per cent.

Tests

Assay—Dissolve 0.5 gram of the powdered sample by warming with 20 cc. of 20 per cent sodium hydroxide solution in a glass-stoppered 250-cc. bottle. Add 2 grams of potassium iodide and when it has dissolved, dilute with 100 cc. of water and add 15 cc. of hydrochloric acid. Allow to stand, protected from light, for 5 minutes. Then titrate the liberated iodine with 0.1 *N* thiosulfate, adding starch solution towards the end. Each cubic centimeter of thiosulfate corresponds to 0.01077 gram $PbCrO_4$.

Note—There are on the market several basic lead chromates of variable composition. The object of the assay is to insure, for reagent purposes, a uniform normal chromate. Moreover, by adopting an assay, the testing for impurities such as chloride, sulfate, etc., which is rather difficult in this instance, can be dispensed with.

Soluble Matter—Boil about 0.5 gram of the powdered sample for 5 minutes with a mixture of 100 cc. of water and 5 cc. of glacial acetic acid, stirring well during the heating. Cool and filter. Evaporate 25 cc. of the filtrate to dryness on the steam bath and dry at 105° to 110° C. Heat 50 cc. of the filtrate with 2 grams of the powdered sample for 5 minutes at 80° to 90° C., cool, dilute to 50 cc., and filter. Evaporate 25 cc. of this filtrate on the steam bath and dry at 105° to 110° C. The difference between the weights of the two residues should not be more than 0.0020 gram.

Carbon Compounds—Heat 4 grams in a stream of carbon dioxide-free air or oxygen in a combustion tube and pass the evolved gas through 10 cc. of saturated barium hydroxide solution diluted to 50 cc. The turbidity should not be greater than is produced in a similar solution of barium hydroxide by 2 cc. of 0.01 *N* sodium carbonate solution.

Lead Nitrate

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Copper (Cu)—To pass test (limit about 0.002 per cent).
Iron (Fe)—Not more than 0.001 per cent.
Substances Not Precipitated by Hydrogen Sulfide (as sulfates)—Not more than 0.10 per cent.

Tests

Insoluble Matter—Dissolve 10 grams in 100 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the insoluble residue should not exceed 0.0005 gram.

Chloride—To a solution of 2 grams in 10 cc. of water, add 5 drops of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion under the same conditions.

Copper and Iron—Dissolve 5 grams in about 40 cc. of water, add 5 cc. of sulfuric acid, evaporate, and heat until fumes of SO_3 are evolved. Cool, mix with about 50 cc. of water, and filter. Wash the precipitate with 15 to 20 cc. of water. Cool the filtrate and divide into two equal portions.

Copper—Bring one-half of the filtrate to a boil, add a slight excess of ammonium hydroxide, and filter. Acidify the filtrate with acetic acid and add 2 cc. of freshly prepared 10 per cent solution of potassium ferrocyanide. No red color should be produced in 10 minutes.

Iron—To the second half of the filtrate, add 2 cc. of hydrochloric acid and 3 cc. of a 10 per cent solution of ammonium thiocyanate. Any red color produced should not be greater than is produced by 0.025 mg. of iron under the same conditions.

Substances Not Precipitated by Hydrogen Sulfide—Dissolve 2 grams in 100 cc. of water and pass hydrogen sulfide through the solution to precipitate the lead completely. Filter, but do not wash. To 50 cc. of the filtrate, add 5 drops of sulfuric acid, evaporate to dryness, and ignite. The weight of the ignited residue should not exceed 0.0010 gram.

Magnesium Oxide

Requirements

Insoluble in Hydrochloric Acid—Not more than 0.030 per cent.
Silica (SiO_2)—Not more than 0.020 per cent.
Ammonium Hydroxide Precipitate—Not more than 0.020 per cent.

Chloride (Cl)—Not more than 0.010 per cent.
Nitrate (NO_3)—To pass test (limit about 0.005 per cent).
Sulfate and Sulfite (SO_4 and SO_3)—Not more than 0.010 per cent as SO_4.
Barium (Ba)—To pass test (limit about 0.005 per cent).
Calcium (Ca)—To pass test (limit about 0.05 per cent).
Heavy Metals (as Pb)—Not more than 0.005 per cent.
Ammonium Sulfide Metals (as Fe)—Not more than 0.01 per cent.
Soluble in Water—Not more than 0.50 per cent.
Loss on Ignition—Not more than 10 per cent.

TESTS

Insoluble in Hydrochloric Acid—Dissolve 5 grams in 100 cc. of water and 25 cc. of hydrochloric acid. Boil for 5 minutes, filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0015 gram.

Silica—Neutralize the filtrate from the determination of matter insoluble in hydrochloric acid with ammonium hydroxide, using methyl red as the indicator, and add 1 cc. in excess. Heat the solution to boiling, boil for a few minutes, and allow to cool. (This operation precipitates a small fraction of the magnesium and collects all of the silica, as well as the usual R_2O_3 precipitate.) Filter and discard the filtrate. Dissolve the precipitate from the filter paper by dropping over it hot dilute hydrochloric acid (1 + 1), finally washing out all soluble salts into the original beaker and retaining any insoluble matter on the filter. Add 5 cc. of sulfuric acid and evaporate the solution to fumes. Cool, dilute with water, and filter through the paper previously used. Wash, ignite, and weigh. Treat the ignited precipitate with a few drops of sulfuric acid and hydrofluoric acid. Evaporate off the hydrofluoric acid, ignite, and weigh. The weight of silica should not exceed 0.0010 gram.

Ammonium Hydroxide Precipitate—To the last filtrate from the silica determination add a slight excess of ammonium hydroxide and boil gently in a covered beaker till the excess of ammonia is expelled. Filter, wash thoroughly, and ignite. The weight of the ignited precipitate should not exceed 0.0010 gram.

Chloride—Add 0.5 gram of the sample to a mixture of 100 cc. of water and 3 cc. of nitric acid. Filter if necessary, dilute to 25 cc., and add 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced should not be greater than is produced by 0.05 mg. of chloride in an equal volume of solution containing the quantities of reagents used in the test.

Nitrate—In a mixture of 1 gram of the sample and 15 cc. of water, dissolve 50 mg. of sodium chloride, add 2 drops of indigo solution (1 in 1000) and add slowly with constant stirring 15 cc. of sulfuric acid. The color should not be destroyed in 5 minutes.

Sulfate and Sulfite—Moisten 10 grams with 50 cc. of water and dissolve by adding 45 cc. of hydrochloric acid and boiling. Filter and neutralize the filtrate with ammonium hydroxide, using methyl red as indicator. Dilute to 200 cc., add 5 drops of bromine water and 2 cc. of hydrochloric acid. Heat to boiling, add 20 cc. of 10 per cent barium chloride solution. Heat on the steam bath 3 or 4 hours, and set aside for 36 hours. Filter, wash thoroughly, ignite, and weigh. The weight of the ignited precipitate should not be more than 0.0025 gram greater than the precipitate obtained by running a blank, including filtration, using the quantities of reagents used in the test. Most of the hydrochloric acid in the blank should be removed by evaporation before neutralization with ammonium hydroxide.

Barium—Dissolve 2 grams in a mixture of 16 cc. of water and 10 cc. of hydrochloric acid, and filter. To one-half the filtrate add 1 cc. of *N* sulfuric acid. There should be no difference in turbidity of the two portions at the end of 30 minutes.

Calcium—Mix 1 gram with 4 cc. of water and add hydrochloric acid drop by drop till the oxide is just dissolved. Dilute with water to 10 cc. and filter if necessary. Mix 5 cc. of the solution with 50 cc. of 95 per cent alcohol, add 20 cc. of dilute sulfuric acid (1 + 5), and allow to stand overnight. No precipitate or turbidity should be produced. If crystals are formed warm the solution slightly.

Heavy Metals—Mix 1 gram with 20 cc. of water and add hydrochloric acid (about 5 cc.) until the oxide is dissolved. Neutralize to litmus paper with ammonium hydroxide. Add 3 drops of glacial acetic acid, dilute to 50 cc., and pass hydrogen sulfide through the solution. Any dark color produced should not be greater than is produced by 0.05 mg. of lead in a solution of the same acidity containing the quantities of reagents used in the test.

Ammonium Sulfide Metals—Moisten 1 gram with 20 cc. of water, add 5 cc. of hydrochloric acid, and heat until the oxide is dissolved. Make the solution alkaline to litmus paper with ammonium hydroxide, and add 5 cc. of hydrogen sulfide water. Any green or brown color should not be deeper than the green color produced by 0.10 mg. of iron in an alkaline sulfide solution.

Soluble in Water—Heat to boiling 2 grams of the sample with 50 cc. of water and filter while hot. Evaporate 25 cc. of the filtrate to dryness on the water bath and ignite gently. The weight of the residue should not exceed 0.0050 gram.

Loss on Ignition—Ignite about 0.25 gram in a covered platinum crucible at a bright red heat for 15 minutes. The loss should correspond to not more than 10 per cent.

Mercuric Chloride

REQUIREMENTS

Non-Volatile Matter—Not more than 0.020 per cent.
Solution in Ether—To pass test.
Iron (Fe)—Not more than 0.002 per cent.

TESTS

Non-Volatile Matter—Ignite 5 grams with 1 cc. of sulfuric acid. The weight of the residue should not exceed 0.0010 gram.

Solution in Ether—Two grams of mercuric chloride should dissolve in 60 cc. of ether without leaving an insoluble residue.

Iron—Dissolve the residue obtained in the test for non-volatile matter by warming with 1 cc. of hydrochloric acid. Dilute with 20 cc. of water, add 2 cc. of hydrochloric acid and 2 cc. of 10 per cent ammonium thiocyanate solution. The red color should not be more than is produced by 0.1 mg. of ferric iron under the same conditions.

Mercurous Chloride

REQUIREMENTS

Non-Volatile Matter—Not more than 0.020 per cent.
Mercuric Chloride ($HgCl_2$)—Not more than 0.01 per cent.
Sulfate (SO_4)—Not more than 0.01 per cent.

TESTS

Non-Volatile—Ignite 5 grams with 1 cc. of sulfuric acid. The weight of the residue should not exceed 0.0010 gram.

Mercuric Chloride—Shake 1 gram with 10 cc. of alcohol for 5 minutes, and filter. To 5 cc. of the filtrate, add 2 drops of hydrochloric acid and 5 cc. of hydrogen sulfide water. Any darkening produced should not be greater than is produced by 0.05 mg. of mercuric chloride in a mixture of 5 cc. of alcohol, 2 drops of hydrochloric acid, and 5 cc. of hydrogen sulfide water.

Sulfate—Digest 2 grams for 10 minutes with 20 cc. of a mixture of equal volumes of hydrochloric acid and water. Filter, add 0.01 gram of sodium carbonate to one-half of the filtrate, and evaporate to dryness on the steam bath. Treat the residue with 0.5 cc. of dilute hydrochloric acid (1 + 4), dilute to 10 cc., and add 0.5 of 10 per cent barium chloride solution. Any turbidity should not be greater than is produced by 0.1 mg. of SO_4 under the same conditions.

Sodium Nitroferricyanide

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.030 per cent.
Sulfate (SO_4)—To pass test (limit about 0.01 per cent).

TESTS

Insoluble Matter—Dissolve 5 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the insoluble residue should not exceed 0.0005 gram.

Chloride—Dissolve 2 grams in 175 cc. of water, add 2.5 grams of copper sulfate crystals (free from chloride) dissolved in 25 cc. of water, mix thoroughly, allow to stand till the precipitate has settled and filter, rejecting the first part of the filtrate. To 10 cc. of the filtrate, add 2 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity should not be greater than is produced by 0.03 mg. of chloride under the same conditions.

Sulfate—Dissolve 5 grams in 100 cc. of water without heating, filter, and to the filtrate add 5 drops of glacial acetic acid and 5 cc. of 10 per cent barium chloride solution. Stir and pour into a Nessler tube for observation. No turbidity should be produced in 10 minutes.

Uranium Nitrate

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.002 per cent.
Sulfate (SO_4)—To pass test (limit about 0.005 per cent).
Alkalies and Alkaline Earths (as sulfates)—Not more than 0.10 per cent.
Heavy Metals—To pass test (limit about 0.002 per cent Pb).
Iron (Fe)—Not more than 0.003 per cent.
Uranous Uranium (U^{IV})—Not more than 0.060 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in 100 cc. of water and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water, add 0.5 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion under similar conditions.

Sulfate—Dissolve 1 gram in 5 cc. of water, add 10 cc. of hydrochloric acid, and evaporate to dryness on the steam bath. Treat the residue with 1 cc. of dilute hydrochloric acid (1 + 4) and 10 cc. of water. Filter if necessary, and add 1 cc. of 10 per cent barium chloride solution. No turbidity or precipitate should be produced in 15 minutes.

Alkalies and Alkaline Earths—Ignite 2 grams until thoroughly decomposed. Powder the cooled residue and boil for 10 minutes with 50 cc. of water. Cool, dilute to 50 cc., mix well, and filter. To 25 cc. of the filtrate add a few drops of sulfuric acid, evaporate to dryness, and ignite gently. The weight of the residue should not exceed 0.0010 gram.

Heavy Metals—Dissolve 2 grams in 5 cc. of water, add 10 cc. of hydrochloric acid, and evaporate to dryness on the steam bath. Treat the residue with 1 cc. of 0.1 *N* hydrochloric acid and 20 cc. of water. Filter if necessary and pass hydrogen sulfide through the solution. No darkening should be observed.

Iron—To a solution of 2 grams in 25 cc. of water, add a solution of 5 grams of ammonium thiocyanate in 10 cc. of water and shake the mixture with 10 cc. of ether. The red color produced in the ether should not be greater than is produced by 0.06 mg. of iron in a ferric salt treated with the quantities of reagents used in the test.

Uranous Uranium—Dissolve 3 grams in 200 cc. of water and add 2 cc. of sulfuric acid. Dissolve and acidify a second equal sample for comparison. Titrate one solution with 0.1 *N* potassium permanganate. Not more than 0.20 cc. of permanganate should be required to cause a color change that can be observed by comparison with the solution not titrated. The 0.20 cc. includes 0.05 cc. allowed to produce the color change in the absence of uranous compounds.

Corrections for Published Specifications

Replace the requirements and tests previously printed by the following:

General Correction for Gravimetric Determination of Sulfate

It has been observed in the determination of sulfate in sodium carbonate that the filter paper retains barium and possibly sodium from the solution passed through it, even though the paper is thoroughly washed. The weight of ash obtained when such papers are ignited may exceed 0.5 mg. For this reason a complete blank determination should be made in all cases in which the permitted weight of barium sulfate is small enough to be affected by an error of the magnitude indicated. In blank determinations in which large amounts of acid are included, as in the case of sodium carbonate, the acidity of the solution should be made to correspond to that of the solution of the sample by evaporation of the excess of acid. This general provision for blanks on sulfate determinations applies to the following reagents:

Citric acid (*5*)
Oxalic acid (*1*)
Perchloric acid (*2*)
Phosphoric acid (*4*)
Tartaric acid (*5*)
Ammonium phosphate (dibasic) (*3*)
Ammonium thiocyanate (*1*)
Bromine (*6*)
Calcium carbonate (*7*)
Calcium carbonate, low in alkalies (*7*)
Calcium chloride ($CaCl_2.2H_2O$) (*7*)
Cupric oxide, powdered and granular (*6*)
Cupric oxide, wire form (*7*)
Cupric ammonium chloride (*6*)
Carbon tetrachloride (*4*)
Potassium bromate (*3*)
Potassium bromide (*3*)
Potassium carbonate (*2*)
Potassium chloride (*2*)
Potassium dichromate (*1*)
Potassium ferricyanide (*5*)
Potassium ferrocyanide (*5*)
Potassium hydroxide (*1*)
Potassium iodate (*3*)
Potassium iodide (*3*)
Potassium permanganate (*2*)
Potassium sodium tartrate (*6*)
Sodium acetate (*3*)
Sodium bicarbonate (*2*)
Sodium carbonate (*2*)
Sodium hydroxide (*1*)
Sodium nitrate (*4*)
Sodium oxalate (*1*)
Sodium peroxide (*4*)
Sodium phosphate (dibasic) (*4*)
Zinc chloride (*5*)

Acid Phosphoric (*4*)

TEST

Heavy Metals—Dilute 3 cc. with 10 cc. of water and exactly neutralize with ammonium hydroxide, using 3 drops of 1 per cent phenolphthalein solution as indicator. Add 50 cc. of 1 *N* sulfuric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color which is immediately developed should not be greater than is produced by 0.05 mg. of lead in the same volume of an aqueous solution of a lead salt treated with the same amount of hydrogen sulfide water.

Ammonium Phosphate (Dibasic) (*3*)

TEST

Heavy Metals—Dissolve 5 grams in 40 cc. of water, add 40 cc. of 1 *N* sulfuric acid, 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color which is immediately developed should not be greater than is produced by 0.05 mg. of lead in the same volume of an aqueous solution of a lead salt treated with the same amount of hydrogen sulfide water.

Barium Carbonate (*3*)

REQUIREMENT

Nitrate (NO_3)—To pass test (limit about 0.01 per cent).

TEST

Nitrate—To 3 grams add 15 cc. of water and 1 drop of indigo solution (1 in 1000), dissolve by adding 5 cc. of hydrochloric acid, and add with constant stirring 15 cc. of sulfuric acid. The blue color should not be destroyed in 5 minutes.

Magnesium Chloride (*5*)

REQUIREMENT

Barium (Ba)—To pass test (limit about 0.005 per cent).

Potassium Ferricyanide (*5*)

Potassium Ferrocyanide (*5*)

TESTS

Chloride—Instead of filtering, allow the precipitate to settle in a cylinder and take 50 cc. of the clear supernatant solution for the test with nitric acid and silver nitrate.

Sulfate—Omit last two sentences.

Potassium Phosphate (Monobasic) (*4*)

TEST

Heavy Metals—Dissolve 5 grams in 40 cc. of water and exactly neutralize with ammonium hydroxide using 3 drops of 1 per cent phenolphthalein solution as indicator. Add 40 cc. of *N* sulfuric acid, 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color which is immediately developed should not be greater than is produced by 0.05 mg. of lead in the same volume of an aqueous solution of a lead salt treated with the same amount of hydrogen sulfide water.

Sodium Bicarbonate (*2*)

TEST

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—In line 5, replace "Allow to stand for 3 hours" with "Stir well and allow to stand overnight."

Sodium Phosphate (Dibasic) (*4*)

TEST

Heavy Metals—Dissolve 5 grams in 40 cc. of water and exactly neutralize the solution with 1 *N* sulfuric acid, using 3 drops of 1 per cent phenolphthalein solution as indicator. Add 15 cc. of 1 *N* sulfuric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color which is immediately developed should not be greater than is produced by 0.05 mg. of lead in the same volume of an aqueous solution of a lead salt treated with the same amount of hydrogen sulfide water.

Sodium Thiosulfate (*2*)

REQUIREMENT

Sulfate and Sulfite—Not more than 0.10 per cent as SO_4.

TEST

Sulfate and Sulfite—Dissolve 1 gram in 50 cc. of water, add approximately 0.1 *N* iodine till the liquid has a faint yellow color. Make to a volume of 100 cc., and mix thoroughly. To 5 cc. of the solution add 5 cc. of water, 1 cc. of 0.1 *N* hydrochloric acid, and 1 cc. of a 10 per cent solution of barium chloride. Any turbidity should not be greater than is produced by 0.05 mg. of SO_4 under the same conditions.

Specifications Previously Published

(1) Committee on Analytical Reagents, IND. ENG. CHEM., **17**, 756 (1925).
(2) *Ibid.*, **18**, 636, 759 (1926).
(3) *Ibid.*, **19**, 645 (1927).
(4) *Ibid.*, **19**, 1369 (1927).
(5) *Ibid.*, **20**, 979 (1928).
(6) *Ibid.*, Anal. Ed., **1**, 171 (1929).
(7) *Ibid.*, **2**, 351 (1930).

According to a report of the Central Drug Department of the Soviet Government, there are forty pharmaceutical producing plants under the control of the local pharmacy administrations. Last year seventy different state organizations furnished medical stores and supplies, which were distributed to them from a central department. Manufacturers of medicinals in Russia are reported as supplying the greater part of the domestic consumption.

A New Test for the Halogens[1]

H. Earl Tremain

Oak Dale Drive, Salina, Kan.

WHILE working with *p*-aminodimethylaniline, it was found that it gave a very sensitive color reaction with an uncombined halogen.

This compound may be obtained by the decomposition of methyl orange by hydrogen sulfide. An easier method is to purify the technical product obtainable in the market. This is done by simply distilling the crude material to remove the colored impurities that would mask the reaction.

p-Aminodimethylaniline is a light brown crystalline substance, melting at 41° C. and boiling at 262° C. It is soluble in water, alcohol, ether, and chloroform, and darkens and decomposes upon exposure to light, air, and moisture.

To prepare the reagent, dissolve 5 grams of *p*-aminodimethylaniline in 100 cc. of absolute alcohol. The alcohol permits less decomposition than water if used as the solvent.

To make the test, 2 or 3 drops of the reagent are added to 5 cc. of water and the solution to be tested slowly added. Only enough should be introduced to produce a clear pink color, or other confusing colors may result. For example, if a 0.01 per cent solution of bromine be added a drop at a time to 5 cc. of the reagent, the following colors will appear in turn: pink, red, purple, violet-red, green, brown, and yellow, all definite colors formed by the successive halogenation of the benzene nucleus and the methyl side chains in quite a complex manner. The reagent when properly used will detect

1 part Br in 1,300,000 of water
1 part Cl in 65,000 of water
1 part I in 400,000 of water

A convenient though less sensitive method of making the test is with test papers made by dissolving 10 cc. of *p*-aminodimethylaniline in 100 cc. of absolute alcohol. A good grade of filter paper is immersed in this solution and dried. It is then cut into small strips, a strip dropped into 5 cc. of water, and the solution to be tested slowly added. Both the strips and the reagent must be kept in dark, tightly stoppered bottles.

The test should be made in a neutral or slightly acid solution, as an excess of acid will destroy the color, whereas a large amount of alkali would combine with the halogen.

[1] Received November 7, 1930.

NOTES AND CORRESPONDENCE

Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration

Editor of Industrial and Engineering Chemistry:

In a paper under this title, Piccard, Peterson, and Bitting [Ind. Eng. Chem., Anal. Ed., **2**, 294 (1930)] record the results of their investigation of the method of determination of oxides of nitrogen published by us in the *Analyst*, **50**, 262 (1925). In summarizing their conclusions they say:

> We have investigated the Francis and Parsons method thoroughly, but have found that it is not possible to obtain satisfactory results by it unless a blank is subtracted to account for the impurity of the hydrogen peroxide. On the other hand, after modifying the method as described, we were able to obtain results of higher accuracy, without the use of a blank.

(1) It might be inferred from the paragraph quoted above that in our method no account was taken of the possible presence of determinable nitrogen in the reagents used and in the air of the room, and, further, that when this is done, the proportion of such nitrogen found is relatively large. Such inference is entirely wrong. The performance of a blank is an integral part of our method; the magnitude of this blank, as stated in our paper (page 267), never exceeded 0.0015 mg. of nitrogen.

(2) In the modification now proposed by Piccard, Peterson, and Bitting, standards are prepared each time by the same process as that used in the actual analysis. If this is done with all the reagents used in the analysis, full compensation is obtained for the quantity of determinable nitrogen in the reagents and in the air of the room. But the magnitude of this compensation is not determined. It appears to us that the prudent chemist will desire to have this information. Incidentally it may be mentioned that the directions given by Piccard, Peterson, and Bitting for the preparation of our absorbing and oxidizing solution are not those given by us. The quantity of this solution used for each analysis as stated by them, while having an equivalent oxidizing power, contains nearly six times the quantity of sulfuric acid used by us.

(3) We think that a fair view of Piccard, Peterson, and Bitting's paper is that it confirms the accuracy of our method within the limits claimed—namely, that of color comparison in Nessler tubes, which is usually taken to be 5 per cent. In addition, the paper shows that our method may be modified so as to be suitable for use with gas mixtures containing halogen compounds which might be fixed in the solution used for absorbing the oxides of nitrogen.

A. G. Francis
A. T. Parsons

Government Laboratory
London, W. C. 2, England
November 25, 1930

. . . . . .

Editor of Industrial and Engineering Chemistry:

To the three points raised by Francis and Parsons, we should like to reply as follows, making it clear from the beginning that we have in no way the intention of belittling the work of these authors.

(1) The paper of Francis and Parsons was, at the time we started our work, the only paper on which we could rely in order to get results at all. We found, however, that for our purpose certain modifications were necessary. We were not able to secure any hydrogen peroxide of sufficient purity to allow us to use such a great excess as Francis and Parsons did. They use 0.07 of 50 ml. of a $7^1/_2$ per cent hydrogen peroxide solution which makes about 0.3 gram of hydrogen peroxide. We found

that if we use 100 times less hydrogen peroxide, which is still considerably in excess of the theoretical amount, we get a complete oxidation and we need no longer be very particular as to the purity of the reagent. One should certainly not infer from our paper that Francis and Parsons did not use a blank. We intended only to say that for our conditions we should need a blank, and that we prefer to use directions which make such a blank unnecessary for us.

(2) We agree with the letter of Francis and Parsons that the "prudent chemist will desire to have this information"—that is, the knowledge of the magnitude of the errors which are compensated by our method of making a new standard for every analysis. Although we do not mention it in our paper, we have made many blanks before we were able to obtain consistently good results.

As to the statement of Francis and Parsons that we used nearly six times more sulfuric acid than they did, there was indeed an error on our part. It was produced by the following circumstances:

At the start of our work we tried to duplicate as well as possible the work of Francis and Parsons. On page 266, they write that they use for each experiment 7 ml. of a mixture containing 1 ml. of 2 *N* sulfuric acid in 100 ml. of solution. From this we calculated that they used 0.14 ml. of 1 *N* sulfuric acid in each experiment. On page 267, they write that in each experiment the solution was made just alkaline by the addition of 0.5 to 1.0 ml. of 1 *N* potassium hydroxide. Since we did not understand the reason for this difference, we took such an amount of sulfuric acid as would be neutralized by 0.8 ml. of 1 *N* potassium hydroxide. We were in this way following at least the spirit of the publication of Francis and Parsons. When writing our paper, we unfortunately failed to quote the original text of Francis and Parsons. We quoted the directions which we were using, having forgotten that we had made this alteration. We are sorry for this mistake.

From the letter of Francis and Parsons, it is evident that there was no mistake in their publication. It may be interesting, therefore, to find out why they needed 0.5 to 1.0 ml. of 1 *N* potassium hydroxide in order to neutralize a solution to which they had added only 0.14 ml. of 1 *N* sulfuric acid.

The explanation lies, we believe, in the fact that Francis and Parsons used their method for the analysis of combustion gases which contain carbon dioxide and sulfur dioxide. Assuming 20 per cent carbon dioxide in the fume gases (which is the theoretical maximum) and assuming 5.5 per cent sulfur in the coal, we find that 7 ml. of the aqueous oxidizing solution will absorb carbon dioxide equivalent to 0.07 ml. of 1 *N* potassium hydroxide, whereas the sulfuric acid produced by oxidation of 1 liter fume gas will need 0.38 ml. of 1 *N* alkali. Furthermore, we need about 0.03 to 0.05 ml. of normal alkali in order to get a good alkaline reaction toward litmus paper. This makes altogether:

0.14 ml. 1 *N* KOH for neutralization of added H_2SO_4
0.07 ml. 1 *N* KOH for neutralization of CO_2
0.38 ml. 1 *N* KOH for neutralization of H_2SO_4 from sulfur
0.05 ml. 1 *N* KOH excess
0.64 ml. 1 *N* KOH

This amount of potassium hydroxide is well within the limits stated by Francis and Parsons.

This shows that in our case we were justified in adding considerably more sulfuric acid than Francis and Parsons used in order to make the oxidation in a solution of about the same acidity. We did not, however, realize at the time why we had to add more sulfuric acid, and we failed to indicate in our paper that the directions, which we said were the ones of Francis and Parsons, had been modified by us.

(3) It is perfectly right to say that we confirmed the accuracy of the method of Francis and Parsons within the limits claimed by these authors—that is, 5 per cent.

We may even say more than this. Our work has shown that the acid absorption and oxidation of nitrogen peroxide as discovered by Francis and Parsons enable us to reach an unusually high accuracy. As described in our paper, we found in sodium nitrite (present 0.02 mg. of nitrogen) in seven consecutive experiments, 101, 101, 103, 101, 101, 98, and 101 per cent of the theory, and in eight consecutive nitrogen oxide determinations (present about 0.045 mg. of nitrogen), we found 101, 101, 100, 98, 100, 102, 102, and 98 per cent of the theory. In dynamite fumes especially low in nitrogen peroxide, we found successively 95.1, 102.3, 102.3, 95.1, and 105.2 per cent of the average, and in dynamite fumes of ordinary composition, we found 99, 102, 98, 102, and 99 per cent of the average. For these 25 determinations our average error is 1.9 per cent.

J. Piccard
Ernest G. Peterson
C. D. Bitting

Hercules Powder Company
Kenvil, N. J.
January 12, 1931

A Study of the Official Method of Bleaching Test of the American Oil Chemists' Society

Editor of Industrial and Engineering Chemistry:

We are sorry that Ma and Withrow [Ind. Eng. Chem., Anal. Ed., **2**, 374 (1930)] used the expression $\frac{100\,(T-L)}{100-L}$ as a measure of the degree of bleach.

According to Lambert's and Beer's laws, the concentration of coloring matter in a liquid is proportional to the negative logarithm of the amount of light transmitted by the liquid.

Tables of color units based on the amount of light transmitted by a liquid are given by Meade and Harris [J. Ind. Eng. Chem., **12**, 687 (1920)] and by Peters and Phelps [Bur. Standards, *Tech. Paper* **338** (1927)]. Using such systems of units, Teeple and Mahler [Ind. Eng. Chem., **16**, 498 (1924)] have shown that the action of adsorbents on oils follows Freundlich's equation for a while and then the line breaks.

In our work we have never found such a break in the case of aqueous solutions, but have invariably found it in the case of vegetable oils, whether using fuller's earth, activated carbon, or mixtures of these bleaching agents.

Using the data for the green in Table III of the article by Ma and Withrow, and the color units for green which appear in *Chem. Met. Eng.*, **28**, 541 (1921), Table I, we find that the points representing 1 to 4 per cent, inclusive, of fuller's earth follow Freundlich's equation and that the break in the isotherm appears between the points representing 4 and 5 per cent earth.

The use of the Meade-Harris color units for the concentration terms in Freundlich's equation enables one to predict the action of fuller's earth or carbon on a vegetable oil from a few experimentally determined points. We hope that investigators of the action of adsorbents on oils will use this method of reporting their results.

The use of color units proportional to the logarithm of the transmission has the advantage that such units can be converted to Lovibond red units by a factor.

M. T. Sanders

Atlas Powder Company
Wilmington, Del.
November 14, 1930

Correction—In the article "Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid," by Hobert H. Willard and R. C. Gibson, Ing. Eng. Chem., Anal. Ed., **3**, 88 (1931), the number 50.66, on page 89, line 15, of the first column, should read 51.66.

Analytical Edition

Industrial and Engineering Chemistry

Published by the American Chemical Society

Volume 3 JULY 15, 1931 Number 3

Two Hundred Reagent Chemicals—Good and Bad[1,2]

Edward Wichers, Aaron Isaacs, and Irl C. Schoonover

BUREAU OF STANDARDS, WASHINGTON, D. C.

Two hundred and thirty-six lots of reagent chemicals purchased by the Bureau of Standards in the period July 1, 1928, to December, 1930, were examined for conformity to the specifications of the American Chemical Society, or, in the absence of such specifications, for conformity to the requirements indicated by the producers' labels. Although few of them were excessively bad, a large proportion of the chemicals failed to conform fully to the requirements.

Except for the small group of insoluble products, which was much more unsatisfactory than the others, no striking differences in quality between various types or groups of chemicals were noted. In general, the chemicals examined conformed less satisfactorily to the producers' standards than to the American Chemical Society specifications. Considerable differences were found in the success of the producers represented in this review in meeting the requirements of the specifications or of their own standards. Reliance on labels as a definition of quality would not have been fully justified for any of the brands and would have been very unsafe for some.

The results indicate the necessity for the continued development of adequate quantitative methods of test, the critical use of such tests by numerous individuals so as to insure and confirm their adequacy, and the consistent application of the improved standards and tests by producers, under the stimulus of the interest and demands of consumers.

DURING the last few years, the AMERICAN CHEMICAL SOCIETY, through its Committee on Analytical Reagents, has prepared specifications for a considerable number of the analyst's most important reagent chemicals. These specifications purport to provide carefully considered standards of quality which are designed to meet the requirements of careful analytical work without making excessive demands on the ability of the producer of reagents, or necessitating excessively high prices for the reagents. Furthermore, the specifications contain complete methods of test, which are much more quantitative in character than any which have appeared in similar standards. For these reasons and because producers generally have shown themselves willing to sell their materials on the basis of the specifications in question, these new standards of quality offer an excellent common ground of understanding for the producer and consumer of reagent chemicals. Up to date about one hundred specifications have been adopted by the SOCIETY, covering most of the reagents in very general use, and representing in value probably much more than 75 per cent of the cost of all chemicals bought for analytical use. Of approximately $23,000 reported as spent for reagent chemicals bought during the fiscal year 1930 by government laboratories in Washington from the Schedule of the General Supply Committee, 84 per cent was for the 74 items which were purchased under AMERICAN CHEMICAL SOCIETY specifications.

Following fairly extensive, but not entirely systematic, testing of reagent chemicals in earlier years, the Bureau of Standards began in July, 1928, to test all its purchases of such materials. At that time 62 of the SOCIETY's specifications were in force in the annual contracts let by the General Supply Committee. Up to December, 1930, the end of the period for which results of tests are given in this paper, 19 additional specifications went into effect, making a total of 81 specifications in force during part or all of the $2^1/_2$-year period.

The purpose of the Bureau's testing of reagent chemicals is twofold. The work is done both as a matter of self-protection, to insure the work of the analytical laboratories so far as possible from faults caused by poor reagents, and to gain information about the purity of reagents on the market which may be useful in helping to improve the quality of the materials available for the American chemist. Although the total number of lots of material (236) on which this report is based is not very large, the number is sufficient to throw some light on the general question of the purity of present-day reagents.

Classification of Chemicals Tested by Types

The 236 lots of material include 173 bought under the SOCIETY's specifications, which will be referred to as Group I, and 63 bought on the general specification "analytical reagent quality," to be known as Group II. Some of Group II are materials for which specifications came into effect during the $2^1/_2$-year period but were not in effect at the time of purchase. For this reason a few items are represented in

[1] Received May 7, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

both groups. All told, the 236 lots of material represent 93 different reagents. Group I represents 61 items, with purchases for individual chemicals ranging from one to twelve lots. Group II represents 36 items, with a maximum of 8 lots of a single material.

Tests of chemicals in Group I were, of course, made according to the requirements and methods prescribed by the specifications. Materials in Group II were tested for conformity to the producer's own standards—that is, the labels on the containers. The labels of one producer are stated to represent actual analyses of the contents. For the purposes of our records, however, they were regarded as indicating maximum limits of impurities, the practice followed by the other producers whose materials were tested. That is, a material supplied by this producer which was better in one or more respects than the label indicated was not classified as unsatisfactory, although it may not have been correctly labeled. The methods used in testing Group II were taken from various sources, such as Krauch (*3*) or Murray (*4*), or the published methods of the producers.

Any classification of reagent chemicals is necessarily arbitrary. However, dividing them into certain broad groups may be justifiable. Partly in order to furnish a basis of comparison with the purity of reagent chemicals some years ago, the grouping adopted by Buc (*1*) is followed in this paper. Accordingly, the chemicals are listed in Table I under the following types: liquid inorganic chemicals; liquid organic chemicals; soluble compounds of ammonium, potassium, and sodium (ammonium hydroxide is included with the "liquid inorganic chemicals"); other soluble salts; and insoluble products. The chemicals are divided into three classes: Class A represents those that conformed in all respects to the specifications, in the case of Group I, or to the label, in the case of Group II. Class B comprises those chemicals which failed to conform to the specification or to the label in only one respect and by only a relatively small amount. Specifically, if a chemical contained not more than twice as much of one impurity as the specification permitted or the label indicated, it was placed in Class B. Class C comprises those chemicals which departed from the specification or the label in more than one respect, or in a single respect by more than 100 per cent. This method of grading is about equivalent to "good, fair, and bad." To facilitate consideration the figures for the classes are given in percentages of the total number of lots tested in each group and type. Percentages do not mean much in cases in which only a very few chemicals were tested, but they are given throughout for the sake of uniformity.

It will be observed that only 65 per cent of all the lots of reagents bought in the $2^1/_2$-year period conformed strictly to the standards, either the specifications or the producers' labels. If the limits are liberalized so as to include the fair samples with the good ones, the percentage of acceptable materials is raised to 74. The percentage of samples conforming to the producers' own standards (as indicated by the labels) is somewhat less than the percentage conforming to the Society's standards. No doubt some allowance should be made for the fact that the materials in Group II are less commonly used and probably less important than those in Group I. Nevertheless, in view of general representation by producers that labels can be accepted at their face value, a failure in reliability of 41 per cent should not be regarded too lightly. The relatively small proportion of chemicals in Class B, 10 per cent in Group I and 6 per cent in Group II, as compared with 23 per cent and 35 per cent, respectively, in Class C, indicates that for the most part the failure to conform to the standards is distinct enough not to be accounted for either by too rigid requirements or by uncertainties in the methods of test. Of course, Class C includes many degrees of inferiority. Relatively few of the chemicals examined, possibly 3 per cent of the total, might be termed "very bad."

The results of these tests are in fairly good general agreement with others made previously in this laboratory. Thirty per cent of 115 samples tested in 1922–23, representing nearly all of the reagents purchased during that period, were found unsatisfactory in one or more respects. From 1924 to 1926, 94 samples, representing the more important purchases, were examined, of which 18 per cent were unsatisfactory.

Table I—Classification by Types of Chemicals Tested

Type	Number	Class A	Class B	Class C
		%	%	%
GROUP I				
Liquid inorganic	40	73	7	20
Liquid organic	36	78	14	8
NH_4, K, Na compounds	55	66	7	27
Other soluble compounds	34	65	14	21
Insoluble products	8	25	..	75
Total	173	67	10	23
GROUP II				
Liquid inorganic	1	..	..	100
Liquid organic	19	68	5	27
NH_4, K, Na compounds	14	86	..	14
Other soluble compounds	22	46	8	46
Insoluble products	7	29	13	58
Total	63	59	6	35
GROUPS I AND II COMBINED				
Liquid inorganic	41	71	7	22
Liquid organic	55	75	11	14
NH_4, K, Na compounds	69	70	6	24
Other soluble compounds	56	57	13	30
Insoluble products	15	27	6	67
Total	236	65	9	26

Buc (*1*), reporting on chemicals purchased by the Bureau of Chemistry of the U. S. Department of Agriculture from 1915 to 1919, regarded 150 samples out of a total of 1300 examined, or 11 per cent, as "unsatisfactory," as compared with 35 per cent placed in Classes B and C, or 26 per cent in Class C only, in this paper. Spencer (*5*), reporting on tests made in the Bureau of Chemistry from 1920 to 1923, stated that 32 out of 465 lots, or 7 per cent, were "returned as unfit for the Bureau work." The natural conclusion from this comparison, that the general quality of reagent chemicals is at present worse than in the years 1915 to 1923, is not supported by the experience of the average analyst. As a matter of fact, it is not unlikely that the reverse is true, certainly if only the period covered by Buc's report is considered. The more probable cause of the difference is that both Buc and Spencer reported on routine tests which were made to determine whether the chemicals could be accepted for the work of the Bureau and were interpreted somewhat liberally, whereas the tests reported in this paper were made to determine whether the materials purchased conformed to definite standards. A large part, but not all, of the chemicals listed in Classes B and C were rejected. Furthermore, the improved methods of testing which have become available in recent years, mainly through the work of the Committee on Analytical Reagents, have made it possible to determine the quality of chemicals much more quantitatively than could be done some years ago.

Buc made comments on each of his five types of chemicals. His observation that the insoluble products were generally bad, pretty well describes the situation today, so far as can be judged from the very limited number of samples examined. The quality of liquid organic reagents seems to be better now than it was in 1915–19. Now, as then, less complaint can be made about the common acids, alkalies, and alkali salts than about other inorganic compounds.

Classification by Producers

Inasmuch as nearly three-fourths of the chemicals under consideration were judged according to a common standard, it may be of interest to classify them according to the produc-

ers from whom they were received. There are at present in the United States six principal concerns which are producing reagents. Probably none of these concerns manufactures, or perhaps even refines, all of the materials which it places on the market, but all of them offer a more or less complete line of chemicals for the quality of which they accept responsibility. Four of these six producers were represented either directly, or by jobbers, in the General Supply Committee's contracts for reagent chemicals during the period for which this report is made. There is some tendency to specialization in chemicals, and each concern is apt to gain awards or contracts on its specialties. Partly for this reason, there was relatively little opportunity to compare the quality of particular chemicals from several sources. However, since the classification by types did not disclose any radical differences in quality between the different types, except for the very small group of insoluble products, it is believed that the classification by producers is not inherently unfair to any one of them. A question as to this point might perhaps be raised on behalf of the producer listed as No. 4, who is represented by only 19 lots. Since all of the materials tested were bought on a competitive basis, no differences in price levels are involved.

In addition to the classification according to producers of the chemicals bought on the Society's specifications, Table II also classifies in the same way the chemicals of Group II. So far as it goes, this group offers a means of judging the degree to which the different producers met their own standards. For completeness the two groups are combined in a similar way, so as to offer a picture of any general variation in the reliability of the producers.

Table II—Classification of Chemicals Tested, by Producers

Producers	Number	Class A	Class B	Class C
		%	%	%
		GROUP I		
1	60	76	7	17
2	35	63	14	23
3	39	64	10	26
4	16	44	6	50
All others	23	70	13	17
Total	173	67	10	23
		GROUP II		
1	18	88	..	12
2	28	40	14	46
3	14	57	..	43
4	3	67	..	33
All others	..	..	..	..
Total	63	59	6	35
		GROUPS I AND II COMBINED		
1	78	80	5	15
2	63	52	14	34
3	53	62	8	30
4	19	47	5	48
All others	23	70	13	17
Total	236	65	9	26

Table II shows a sufficient differentation between producers to be of concern to the analyst. Although the relatively small number of lots tested may make the results less significant than they appear, it seems evident that there were distinct differences in the success of the different producers in meeting the standards. It also seems that the strain of meeting the Society's specifications was in some cases less severe than that of making what is behind the label conform to what is printed on the label.

Discussion of Specific Cases

A few specific instances may help to indicate ways in which improvement might be brought about. It was surprising to find, for instance, five out of six lots of sodium bicarbonate failing to meet the specification with respect to impurities indicated collectively as "calcium, magnesium, and ammonium hydroxide precipitate," and limited to 0.01 per cent. The amounts found were from 0.03 to 0.05 per cent. Apparently the cause of this discrepancy lies in the fact that earlier standards did not include limits for magnesium, or, in some cases, for either magnesium or calcium. Hence some of the producers probably have not customarily tested for these impurities.

Somewhat different are the cases of calcium carbonate containing 0.8 per cent of alkali chlorides and labeled "alkalies, 0.03 per cent;" and of seven lots of cobalt nitrate (an original delivery and six successive replacements) labeled "Ni, none, 0.05, 0.20, 0.075, 0.24, 0.24, and 0.03 per cent," and containing 0.39, 0.46, 0.87, 0.50, 0.58, 0.58, and 0.07 per cent of nickel, respectively. In both of these cases the source of trouble lay in grossly inadequate methods of test. In both cases the producers are now acquainted with suitable methods and are in position to supply materials for which the impurities in question can be correctly indicated. These cases illustrate the opportunity that the user has of raising the standards by making constructive complaints to the producers. In connection with the reference to calcium carbonate low in alkalies, it may be noted that while material satisfactory in this respect is now available, it is apt to contain an excessive amount of sulfate.

Examples of materials which must have been tested very carelessly, if at all, are as follows: tartaric acid labeled "non-volatile matter, 0.007 per cent," and containing 0.025 per cent (the Society's specification permits 0.020 per cent); sulfurous acid labeled "non-volatile matter, 0.0001 per cent, sulfuric acid, 0.05 per cent;" and containing 0.0016 per cent and 0.63 per cent, respectively; arsenic trioxide (a primary standard) labeled "non-volatile matter, 0.05 per cent" and containing 0.4 per cent; and benzene marked "boiling point, 80.5° C.," which had a boiling range of 80° to 92° C. An extreme instance was that of bromine containing 6.3 per cent of chlorine but labeled "chlorine, 0.10 per cent." This may have been a simple blunder, as was undoubtedly the instance of sodium nitrite which was about one-third potassium nitrite. Mislabeling of one lot of calcium carbonate as to alkali content was attributed by the producer to a blunder made by confusing two grades of material.

The greater number of less extreme cases which fall into Class C are best explained either by failure on the part of the producers to exercise the constant analytical control which they claim, over their products, or by a combination of inadequate methods and insufficient care in the analytical control. Anyone who has had experience in the testing of chemical reagents for small amounts of impurities knows that methods in this field have been none too good and that even if an adequate method is at hand, competent analysts may occasionally differ considerably in their results. It is exactly in the development of better methods, their critical trial by numerous individuals, and their use by producers in replacement of the more familiar, but less reliable methods, that the means lie for real improvement in the quality of reagent chemicals.

Basis of Possible Improvement

There can be hardly any doubt that most of a general improvement in the quality of reagents can be accomplished only through the interest and activity of the users. It is manifestly cheaper to produce poor chemicals than good ones and the pressure of competition always has to be borne, no matter how much a producer may be interested in the quality of his products. On the other hand, a cardinal principle of business is to supply what is demanded, and reagent makers can and undoubtedly will produce good reagents if there is a genuine demand for them. In the abstract the analyst will always agree that his reagents ought to be good, especially in these days when he is confronted with increasingly greater demands for accuracy in his work, but in the concrete he is usually like the cobbler who is too busy to shoe his own children—he seldom undertakes to analyze his own reagents. If every competent and responsible analyst would spend one

half-day a month in the indoor sport of examining the latest delivery of one of his more important reagents and rejecting the delivery if unsatisfactory, reagent chemicals generally would soon be above reproach and the next generation of analysts would have good cause to bless their benefactors. More than one user, in reply to a question as to what is done with chemicals that are found unsatisfactory, has answered, in effect, "Oh, we throw them away and tell the purchasing agent to buy a new lot from another maker." Incidentally, it may be added that, for the most part, producers have been found very receptive to constructive suggestions and very willing to replace unsatisfactory materials.

It is often claimed that present-day reagents are as good as the users are willing to pay for and that any extensive improvement in quality would involve a prohibitive increase in price. There can be little doubt that some increase in the cost of the chemicals would result from any general improvement in quality. Whether the increase would be so large as to be prohibitive is another question. If the market for reagents should refuse to tolerate prices commensurate with improved quality, it would be different from the market for almost every other commodity. The importance of quality rather than price is emphasized when one compares the cost of the chemicals with the cost of the chemist's time. Figures from four laboratories in Washington, obtained some years ago (*2*), showed that for a given period the cost of chemicals was 2.2 per cent of the salaries of the chemists who used them. It should be possible to make even the proverbially penny-wise purchasing agents see that some increase in this ratio would be justified if the waste of time that results from reagents of poor quality could be avoided.

Analysts whose work counts are willing to pay for quality in balances, burets, and beakers. They will also pay for quality in chemicals when they are convinced that quality is available. The question of cost for a limited number of very extensively used chemicals may have to be answered by providing special grades of these materials for specific uses. For the larger number of chemicals used in smaller quantities for a great variety of uses, it should be feasible to adjust single specifications to the quality demanded by the greater number and more important of such uses. An illustration of this is found in the reagent mineral acids, which are produced in large quantities at a high level of quality and at prices which do not prohibit their use for a great many purposes, for some of which materials of lower quality could well be used. Single grades of these materials at fairly high levels of quality are more economical than numerous grades.

Literature Cited

(1) Buc, H. E., J. Ind. Eng. Chem., **11**, 1140 (1919).
(2) Collins, W. D., "The American Chemist and His Reagents," unpublished address before the Lehigh Valley Section, of the American Chemical Society, Easton, Pa., September 23, 1925.
(3) Krauch, C., "The Testing of Chemical Reagents for Purity," 3rd ed., Van Nostrand, 1902. Translated by J. C. Williamson and L. W. Dupre.
(4) Murray, B. L., "Standards and Tests for Reagent Chemicals," Van Nostrand, 1927.
(5) Spencer, G. C., Ind. Eng. Chem., **15**, 1281 (1923).

A Degree Brix–Total Solid Relationship[1]

Study of Possible Theoretical Brix Correction Factor for Approximation of Solids by Drying Using Carbonate Ash Determination

R. H. King

College of Agriculture, University of the Philippines, Lajuna, P. I.

An investigation involving 1870 samples of final molasses from 31 sugar-producing factories covering a $2^1/_2$-year period has been conducted in order to obtain a possible correction factor for Brix solids so that approximations could be obtained for true total solids.

Average relationships between carbonate ash, Brix solids, and total solids by drying have been obtained. The difference between the Brix solids and the total solids has been evaluated and correlated with the carbonate ash content. Through the use of a correction factor based upon the carbonate ash, a close approximation of the total solids can be obtained.

The relationship between solids by drying and the Brix solids appears to be that of a straight-line function. Total solids may be approximated from these average curves if the carbonate ash content is known. However, if the ash content is not known, the graphs are of value in determining the probable total solids from the Brix solid determination.

It is suggested that carbonate ash determinations be used in connection with Brix solids for the evaluation of the total solids in the chemical control where closer approximations are desired for control purposes.

CHEMICAL control in cane and beet sugar factories is generally based upon the data obtained with a hydrometer known as the Brix spindle. This hydrometer in pure sugar solutions gives the actual solids in solution. In such pure solutions the Brix solids are the so-called true solids, obtained by drying. However, as the non-sucrose material, such as ash, acids, and organic non-sugars, do not influence the hydrometer in the same degree as sucrose, errors enter into the control work when the degree Brix is used instead of the true solids obtained by drying.

A quick ready method of estimating the true solids from the Brix solids is desired. Total recovery, sugar distribution, and the efficiency of the particular factory depend upon the estimation of the dry matter entering the process. The element of time and the expense of obtaining actual solids by drying prohibit an accurate control.

It is well known that the character of the non-sugars, generally inorganic (*2*, *3*), governs the difference between the actual solids and the degree Brix. If ash determinations on average samples of molasses would give a correction factor, then ash determinations could be made in routine control work, and this correction factor applied to the Brix reading would give, at least, a closer approximation of the true solids. The advantage would be that the unsatisfactory method of drying *in vacuo* would be eliminated.

[1] Received October 7, 1930.

Experimental Procedure

The possibility of obtaining such a correction factor was attractive. However, at the beginning it was clearly recognized that any factor determined would not be of universal application; factors must be obtained for each individual producing unit. The investigation was conducted on 1878 separate samples of final molasses from 31 manufacturing units. The samples were analyzed for sucrose, Brix solids by drying, and carbonate ash.

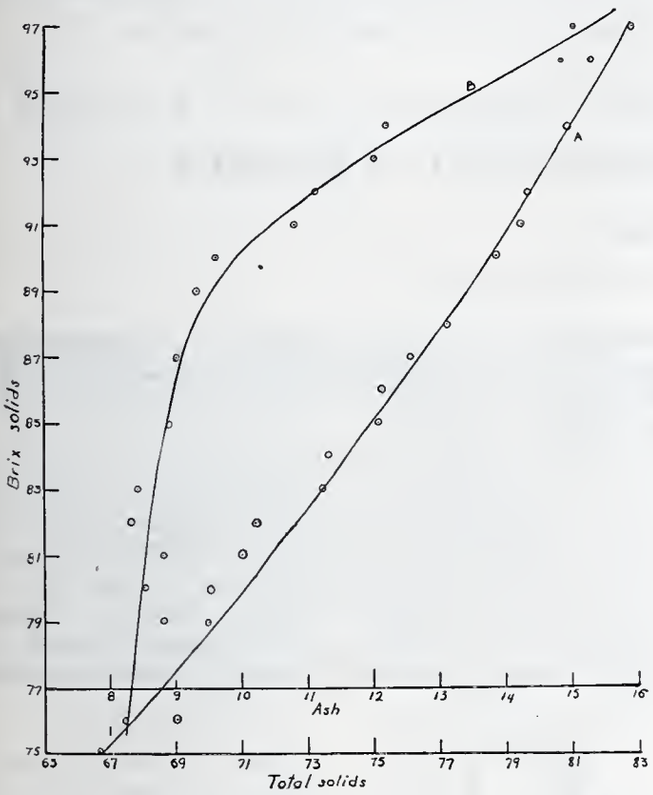


Figure 1—Relationship of Difference between Brix Solids, Solids by Drying, and Carbonate Ash

Sucrose Determination—Sucrose determinations were made in duplicate on 100 grams of molasses diluted to 600 grams with distilled water. All samples were clarified with Horne's dry lead using six grams per one hundred cubic centimeters of molasses solution. The inversion and analytical procedure used were those given in the methods of chemical control for cane sugar factories as used by the Association of Hawaiian Sugar Technologists (*1*).

Brix Solid Determination—The standard method of diluting the final molasses to the approximate Brix solids of the mixed juice was used. Five readings were made on the diluted molasses and the arithmetical average was multiplied by the dilution factor of six. Spindles calibrated at 27.5° C., as certificated by the Hawaiian Sugar Planters' Association, were used.

Solids by Drying—Total solids were determined by drying to constant weight in an aluminum dish which was provided with a tight-fitting cover in a Fries electric oven maintained at 100° C. with a vacuum of 50 mm. of mercury. Twenty-five grams of washed silica sand were used as a spreader for approximately 2 grams of molasses. Ten cubic centimeters of distilled water were added so that the molasses could be well mixed with the sand. A preliminary evaporation was accomplished on a water bath. Duplicate determinations agreed within 0.05 per cent.

Ash Determination—Carbonate ash determinations were made in duplicate on all samples in the following manner: Approximately 4 grams of the sample were weighed into a tared 100-cc. platinum dish and 0.5 gram of pure paraffin was added. The dish was first heated on an asbestos wire gauze over a Bunsen burner to char the organic matter, and ignition was completed in an electric muffle at a temperature below dull redness. About 5 hours were required for a white or gray ash. The ash so obtained was cooled in a calcium chloride desiccator. This method gave determinations which differed by only 0.02 per cent.

Discussion of Results

The results of the determinations of Brix solids, total solids, and the corresponding carbonate ash were averaged arithmetically and arranged in groups according to each degree Brix between 74.5 and 96.5, inclusive, as shown in Table I. The difference between the degrees Brix and the total solids is designated as "theoretical ash."

Table I—Difference between Degrees Brix and Total Solids

Gravity ° *Brix*	Total Solids %	Theoretical Ash[a] %	Actual Ash %	Number Samples
74.5	66.6	7.9	7.8	10
75.5	68.9	8.6	8.2	11
78.5	69.8	8.7	8.8	21
79.5	70.1	9.4	8.5	42
80.5	70.9	9.6	8.8	21
81.5	71.4	10.1	8.3	70
82.5	73.1	9.1	8.4	61
83.5	73.6	9.9	8.7	92
84.5	74.7	9.4	8.9	31
85.5	75.2	10.3	9.0	172
86.5	76.1	10.4	9.0	141
87.5	77.2	10.3	9.2	190
88.5	77.9	10.3	9.3	112
89.5	78.6	10.2	9.6	121
90.5	79.2	11.1	10.8	162
91.5	79.6	11.6	11.1	240
92.5	80.1	12.4	12.0	110
93.5	80.8	12.7	12.6	161
94.5	81.4	13.1	13.4	70
95.5	81.9	14.0	14.3	30
96.5	82.7	14.2	14.4	10
				1878

[a] Degrees Brix minus percentage of total solids.

The average data obtained in this investigation were plotted in order to obtain a general relationship between the difference between the Brix solids, the solids by drying, and the carbonate ash. Curve A of Figure 1 was prepared from the average data of solids by drying and the degrees Brix as given in Table I. A straight line approximately fits these data.

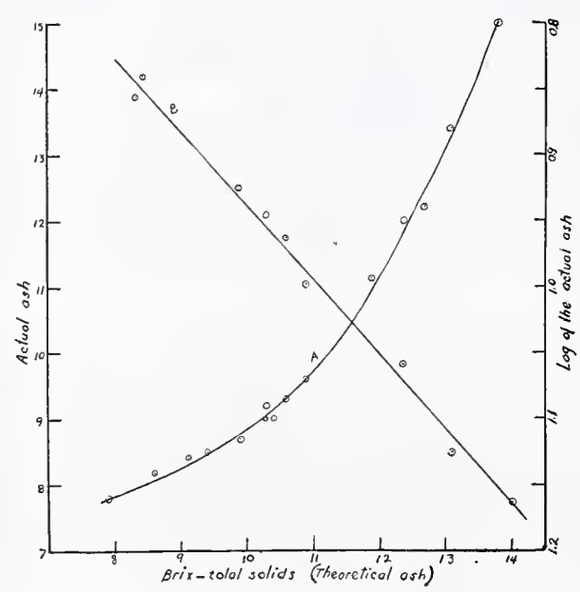


Figure 2—Relationship of Carbonate Ash Content and Difference between Brix and Total Solids by Drying

Curve B of Figure 1, which was also constructed from Table I, shows that the relationship between degree Brix and carbonate ash is not a straight-line function.

In general, the higher the Brix the greater the ash content, though the quantity of ash will also depend upon the purity, and the greater the ash content the greater the divergence

between the Brix reading and the solids by drying. These two curves may be used to estimate the ash content if the degree Brix and solids by drying are known, or, on the other hand, if the ash and degree Brix are known, an average approximation of the total solids can be reached.

In Figure 2 is given the relationship between the carbonate ash content and the difference between Brix and total solids by drying. This latter difference can be considered as a theoretical ash. Curve B of Figure 2 gives the common logarithm relationship of the actual carbonate ash and the theoretical ash. It is seen that the function gives a straight line.

It must be noted that these relationships indicate a general tendency, and no claim is made that these curves are applicable to all conditions. It is believed that they will be of value if only to indicate the magnitude of the error introduced in the chemical control through the use of the Brix solids. It is hoped that the carbonate–theoretical ash relationship will be of value in estimating the true total solids.

Literature Cited

(1) Association of Hawaiian Sugar Technologists, "Methods of Chemical Control for Cane Sugar Factories," Honolulu, Hawaii, 1924.
(2) Browne, "Handbook of Sugar Analysis," Wiley, 1912.
(3) Deerr, "Cane Sugar," pp. 445–9, Norman Rodger, 1921.

Determination of Glycerol in Greases[1]

M. H. Pramme

Chemical Laboratory, Standard Oil Co. of California, Richmond, Calif.

IN THE investigation of the composition of lubricating greases of the usual type—that is, lubricating oils thickened by means of soaps—it is essential to determine whether whole fats, fatty acids, or a mixture of these were used in making the soap. The presence or absence of glycerol, of course, gives the desired information. Three standard methods for the determination of glycerol in various products were investigated, but all were open to certain objections and were unsatisfactory for specific application to the purpose in mind.

The acetin method, in which glycerol is converted into triacetin and subsequently saponified, is the method specified by the American Society for Testing Materials for the determination of glycerol in greases. This procedure requires that the glycerol solution be concentrated to approximately 50 per cent. It is open to the objection that in the analysis of unknown samples it is impossible to tell when this concentration has been reached. If the concentration is much over this figure, glycerol may be volatilized and, if under this figure, the acetin method gives an incorrect figure.

The potassium permanganate method, in which glycerol is oxidized to oxalic acid by alkaline potassium permanganate and then determined as calcium oxalate, gave widely divergent results. The time and temperature seemed to have a varying effect upon the oxidation of the glycerol.

The potassium dichromate method is one in which the aqueous solution of glycerol is oxidized with an excess of standard potassium dichromate and then back titrated with ferrous ammonium sulfate. This titration requires an external indicator and gives good results when one has become accustomed to the end point. However, the method is relatively slow, requiring about $2^1/_2$ hours.

The reaction utilized is as follows:

$$3C_3H_8O_3 + 7K_2Cr_2O_7 + 28H_2SO_4 = 9CO_2 + 40H_2O + 7Cr_2(SO_4)_3 + 7K_2SO_4$$

Since the glycerol is oxidized quantitatively to carbon dioxide by treatment with potassium dichromate, it seemed much simpler and less time-consuming to absorb the carbon dioxide and calculate the glycerol from this. Working along this line, the method described below was adopted with extremely satisfactory results.

Weigh 10 grams of the grease into a 400-cc. beaker and, stirring constantly to avoid bumping, bring to a boil with 75 cc. of 10 N sulfuric acid. Allow to stand on a steam bath until the layers have separated cleanly. This treatment breaks up the soap, the fatty acids dissolving in the mineral oil, the base combining as sulfate, and the glycerol if present remaining in the aqueous layer. The contents of the beaker are now filtered through a doubled wet filter paper, and washed thoroughly with hot distilled water. This treatment removes all the oily material and leaves a clear bright solution.

The oil-free solution containing glycerol is now transferred to the digestion flask which is connected as shown in Figure 1. The tared absorption tower is disconnected and the system flushed for 10 minutes with carbon dioxide–free air, after which it is reconnected and the oxidization of the glycerol started. One hundred cubic centimeters of 50 per cent sulfuric acid saturated with potassium dichromate are added through the separatory funnel, and the contents of the flask are then boiled for 10 minutes, passing carbon dioxide–free air through the system during the boiling. The flushing is continued for 15 minutes after removing the flame. The absorption tower is then weighed and the per cent of glycerol calculated as follows:

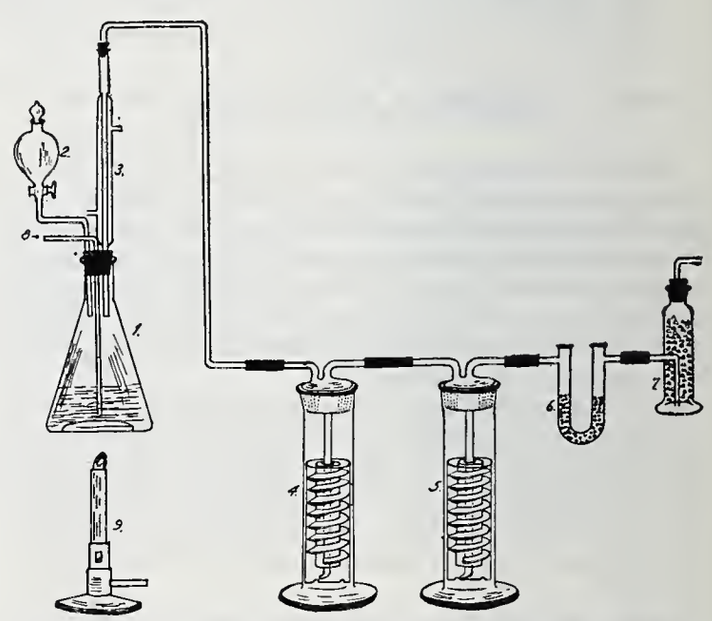


Figure 1—Apparatus for Determination of Glycerol in Greases

1—Digestion flask
2—Separatory funnel containing H_2SO_4 and $K_2Cr_2O_7$
3—Reflux condenser
4—Bubbling tower containing Ag_2SO_4 solution
5—Bubbling tower containing concentrated H_2SO_4
6—U-tube containing $CaCl_2$
7—Ascarite tower for absorption of CO_2
8—Inlet for CO_2–free air
9—Burner

[1] Received October 6, 1930.

$$\% \text{ glycerol} = \frac{\text{weight carbon dioxide} \times 0.6975 \times 100}{\text{weight sample}}$$

In the apparatus the reflux condenser serves to remove chlorine gas or hydrochloric acid, the sulfuric acid and calcium chloride to dry the gas, and the ascarite tower to absorb the carbon dioxide.

Notes—(1) An excess of potassium dichromate must be present. One gram of this salt reacts with 0.134 gram of glycerol.

(2) This method is designed primarily for normal lubricating greases containing soaps, fats, free fatty acids, and mineral oil. If water-soluble organic compounds other than glycerol, which cannot be precipitated with inorganic salts, are present, it cannot be used.

(3) No glycerol is lost in this determination for, according to Lewkowitsch (*1*), glycerol is not volatilized by boiling until the concentration is approximately 30 per cent. The concentration of glycerol in this determination is rarely over 2 per cent.

(4) A determination requires about 3 hours.

Literature Cited

(1) Lewkowitsch, J., "Chemical Technology and Analysis of Oils, Fats, and Waxes," p. 251, Vol. I, Macmillan, 1922.

Use of Wide-Range Indicators for Determination of pH[1]

F. R. McCrumb

W. A. Taylor and Co., Inc., Baltimore, Md.

It has been shown that accurate pH determinations cannot be made on slightly buffered materials with a wide-range indicator when the determinations are carried out with a single solution which may vary considerably in pH from the material being tested.

So-called universal, utility, and range-finding indicators should never be used on such materials as water, soil extracts, paper extracts, beater water, white water, pure sugar liquors, sewage effluents, clay filtrates, brines, flotation feeds, evaporator water, air-conditioning water, laundry rinses, and, in short, any material that is not fairly well buffered, unless it is known definitely that the pH of the indicator does not vary appreciably from that of the sample.

Although fairly accurate results can be secured by using a number of solutions of a wide-range indicator adjusted in steps of 1.0 pH according to the isohydric method, such a procedure offers no advantage over the use of several short-range indicators, with the disadvantage that a wide-range indicator is rarely so sensitive as several short-range indicators used separately because the color changes are not so distinct.

There is a simplicity in the use of a single indicator to cover relatively wide pH ranges that appeals to the practical minded. Consequently, several such indicators have been recommended for pH work and these are being sold under such names as universal, range-finding, and utility indicators. All are prepared by dissolving a mixture of several indicator dyes in a suitable solvent. A number of such mixtures have been described in the literature (*2*).

While several papers have appeared in which the use of wide-range indicators has been advocated, there is a dearth of experimental data on the relative accuracy resulting from their use. It is the purpose of this paper to present some results secured when attempts were made to use a wide-range indicator to determine the pH of such materials as are met with in practice.

The indicator solution employed in this work is one that has become quite popular as a universal or utility indicator. The composition is methyl red, 0.02 per cent; bromothymol blue, 0.04 per cent; thymol blue, 0.04 per cent; and phenolphthalein, 0.02 per cent. The solvent is 60 volumes of specially denatured (No. 30) alcohol diluted to 100 with distilled water. The reaction can be adjusted by adding standard sodium hydroxide solution. The color changes for such a mixture are: pH 3.0, red; pH 4.0, orange-red; pH 5.0, orange; pH 6.0, yellow; pH 7.0, yellow-green; pH 8.0, green; pH 9.0, green-blue; pH 10, violet; pH 11.0, red-violet. Temporary color standards can be prepared from the buffer mixtures of Clark and Lubs in intervals of 0.4 pH over the range 3.0 to 10.0. The proportion of indicator solution to buffer mixture is 0.25 cc. to 5 cc. This enables one to make readings with a relative sensitivity of 0.2 pH.

As soon as a wide-range indicator is applied to practical solutions, the question arises as to the proper pH of the indicator solution. In determining the pH of well-buffered solutions, the pH of an indicator solution is usually of little moment. However, many of the solutions encountered in practice are only slightly buffered, and the reaction of the indicator solution is one of the most important factors to be considered. Quite a few investigators have pointed this out. Birge and Acree (*1*) first suggested the adjustment of the pH of the indicator in steps and treating the weakly buffered unknown solution with indicator approximately isohydric therewith to prevent pH errors. Karracker (*4*), Marsh (*5*), and Pierre and Fudge (*7*) suggested that when working with soil extracts all indicator solutions be adjusted to their respective midpoints. Schlegel and Steuber (*8*) recommended a similar procedure with bromothymol blue when determining the pH of solutions of pure sugars.

In determining the pH of paper, the extracts are invariably only slightly buffered and accurate colorimetric pH results cannot be secured unless care is taken to adjust the pH of the indicator solutions. The data of Wehmhoff (*9*) and of McCrumb and Kenny (*6*) are sufficient to demonstrate this.

Recently Fawcett and Acree (*3*) have published details on their isohydric-indicator method for determining the pH in very dilute solutions and water. This method consists in the use of several solutions of each indicator adjusted to different pH values in 0.2 steps over the range of the indicator. By this procedure it is possible to use an indicator solution having practically the same pH as the unknown solution.

These investigations have proved that the pH of slightly buffered solutions can be determined accurately only when the pH of the indicator solution is reasonably close to that of the unknown sample. For this reason Fawcett and Acree recommended that all indicator solutions, except those used to cover the strongly acid and alkaline ranges, be adjusted to the midpoint of the respective indicator and also to the lowest and highest useful pH values for testing very weak buffers

[1] Received January 30, 1931.

and water. Some commercial firms are now supplying indicator solutions so adjusted in Pyrex bottles.

This question would be of theoretical interest only if it were not that so many of the solutions found in practice are very slightly buffered. Among the most common are the majority of waters, both natural and treated, soil extracts, pure sugar liquors (pan liquors), paper extracts, many beater waters, white water, sewage effluents, clay filtrates, many brines, some flotation feeds, evaporator water, condenser water, air-conditioning water, laundry rinses, etc. It is very important that the colorimetric method be applied in such cases because, owing to low buffer capacity and low conductivity, the pH can rarely be satisfactorily determined by an electrometric method.

It is in the case of such materials that one immediately gets into difficulty when a wide-range indicator is used. Obviously adjustment to the midpoint, pH 7.0, means little if the solution which is being tested is decidedly acid or alkaline. In the case of a short-range indicator like bromothymol blue, if adjustment is made to the midpoint pH 6.8, the greatest variation between indicator and unknown that will be considered is 0.8 pH. If the variation were greater, the sample would be considered as falling outside the range of bromothymol blue and the reading would be disregarded. However, with a wide-range indicator, if one were testing a solution with a pH of 3.0 to 4.0 or 10.0 to 11.0, by using an indicator solution adjusted to pH 7.0 the variation might be 3 or 4 entire pH units. Where the indicator solution may have a lower or higher pH, this variation between indicator and unknown may be even greater than 4 units. It is apparent that such difference must result in incorrect pH readings, except in the case of fairly highly buffered solutions.

Experimental Procedure

In order to determine the magnitude of the errors that may be encountered, several series of pH determinations were carried out by using three separate solutions of the wide-range indicator adjusted to the pH values 5.25, 7.45, and 9.10. These values were determined both by a colorimetric method and by a quinhydrone electrode. In addition, pH determinations were made on each sample by using solutions of short-range indicators adjusted to the respective midpoints. The color standards used were prepared from the buffer mixtures of Clark and Lubs in intervals of 0.2 pH. These were all checked electrometrically. The short-range indicators employed were the sulfonphthaleins of Slagle, White and Acree, Clark and Lubs, and Cohen, together with methyl red and a proprietary indicator, phthalein blue.

Samples were collected and kept in Pyrex vessels. All tests were made in 5-cc. test tubes with a diameter of 11.5 mm. Precaution was taken to avoid variations due to the action of the carbon dioxide of the air. In every case the indicator solution was added to the empty tube and the measured sample pipetted into the tube so that the sample was delivered below the surface as recommended by Fawcett and Acree. Final mixing was secured by gentle stirring with the tip of the pipet.

The form of tabulating the results is uniform throughout the paper and a brief explanation may be useful. In one column are given the pH values as determined by a short-range indicator, in the following columns are found the pH values as determined when wide-range indicator solutions adjusted to different pH values are used, in the last column is found the difference in pH between the results secured with a wide-range indicator solution adjusted to 5.25 and one adjusted to 9.10.

Natural and Treated Waters—The first series of tests was made on a number of samples of natural and treated waters. The results are shown in Table I.

Table I—Determination of pH of Water

Sample	Short-Range Indicators	Wide-Range Indicator with pH of:			
		5.25	7.45	9.10	Max. variation
	pH	*pH*	*pH*	*pH*	*pH*
1[a]	5.8	5.2	6.6	8.6	3.4
2[a]	6.8	5.6	7.0	8.8	3.2
3[b]	7.8	7.2	7.8	8.4	1.2
4[b]	7.6	6.8	7.6	8.4	1.6
5[b]	7.5	6.6	7.4	8.5	1.9
6[b]	7.5	6.6	7.4	8.6	2.0
7[b]	7.8	7.2	7.8	8.4	1.2
8[b]	7.1	6.4	7.2	8.4	2.0
9[b]	7.0	6.4	7.2	8.4	2.0
10[b]	6.9	6.4	7.2	8.4	2.0
11[b]	7.5	7.2	7.6	8.2	1.0
12[c]	10.2	10.0	10.0	10.0	0.0
13[c]	9.8	9.4	9.6	9.8	0.4
14[c]	9.6	9.2	9.4	9.6	0.4
15[c]	9.6	9.0	9.2	9.6	0.6
16[c]	10.0	9.4	9.6	9.8	0.4
17[c]	9.8	9.2	9.4	9.6	0.4
18[c]	9.6	8.6	9.0	9.4	0.8
19[c]	9.6	8.0	8.8	9.4	1.4
20[d]	5.8	5.6	6.0	6.4	0.8
21[d]	6.5	6.4	6.6	6.8	0.4
22[d]	3.0	4.2	4.6	4.8	0.6
23[d]	6.8	6.4	7.0	7.4	1.0
24[d]	6.5	6.2	6.6	7.0	0.8
25[d]	5.4	5.2	5.6	6.0	0.8

[a] Distilled. [b] Drinking. [c] Boiler. [d] Natural.

Paper Extracts—Some pH determinations were made on samples of paper following the extraction method. The extractions were made by gently boiling a mixture of 5 grams of finely divided paper and 250 cc. of distilled water for 1 hour. The total weight of the flask containing the mixture was determined before boiling, and the loss of weight was replaced with boiled distilled water. The mixtures were not filtered, the supernatant extract being withdrawn by means of a pipet for pH determinations. The results are given in Table II.

Table II—Determination of pH of Paper Extracts

Sample	Short-Range Indicators	Wide-Range Indicator with pH of:			
		5.25	7.45	9.10	Max. variation
	pH	*pH*	*pH*	*pH*	*pH*
1[a]	4.2	4.4	4.6	4.8	0.4
2[a]	4.1	4.4	4.7	5.0	0.6
3[b]	4.6	4.6	5.2	5.6	1.0
4[c]	4.7	5.0	5.8	6.5	1.5
5[d]	5.9	6.0	6.6	8.0	2.0

[a] Letter. [b] Yellow copy. [c] Newsprint. [d] Kraft wrapping.

Soil Extracts—Several soils were extracted by using 20 grams of soil and 80 cc. of distilled water. After thorough mixing in Pyrex bottles, the extractions were permitted to settle for 30 minutes and the pH of the supernatant extract determined. The results are shown in Table III.

Table III—Determination of pH of Soil Extracts

Sample	Short-Range Indicators	Wide-Range Indicator with pH of:			
		5.25	7.45	9.10	Max. variation
	pH	*pH*	*pH*	*pH*	*pH*
1[a]	6.4	5.8	6.4	7.4	1.6
2[b]	6.6	6.0	6.8	8.0	2.0
3[c]	6.4	6.0	6.8	8.0	2.0
4[c]	4.8	5.0	5.4	5.6	0.6
5[d]	8.0	7.6	8.0	8.4	0.8

[a] Sandy loam. [b] Heavy loam. [c] Medium loam. [d] Heavy soil.

Table IV—Determination of pH of Laundry Rinses

Sample	Short-Range Indicators	Wide-Range Indicator with pH of:			
		5.25	7.45	9.10	Max. variation
	pH	*pH*	*pH*	*pH*	*pH*
1[a]	5.5	5.4	5.6	6.0	0.6
2[a]	4.2	4.8	5.0	5.4	0.6
3[a]	5.0	5.0	5.4	5.8	0.8
4[b]	7.7	7.2	7.6	8.0	0.8
5[b]	7.4	7.0	7.6	8.0	1.0

[a] After sour. [b] After suds.

Laundry Rinses—Since pH control is now being applied to laundry operations, a few tests were made on samples of rinse waters. The results are shown in Table IV.

Dilute Alum Solutions—The next series of tests was carried out on dilute solutions of paper-maker's alum. The results are given in Table V.

Table V—Determination of pH of Dilute Alum Solutions

Sample	Alum Concentration	Short-Range Indicators	Wide-Range Indicator with pH of: 5.25	7.45	9.10	Max. variation
	P. p. m.	*pH*	*pH*	*pH*	*pH*	*pH*
1	8000	3.8	4.0	4.0	4.0	0.0
2	40	4.6	4.8	5.0	5.2	0.4
3	80	4.4	4.8	5.0	5.2	0.4
4	800	4.0	4.4	4.6	4.6	0.2
5	8	5.0	5.0	5.6	6.8	1.8

Sugar Solutions—In the refining of sugar, as the purity of the liquors increases, they become correspondingly less buffered. Accordingly, pH determinations on highly purified char-filtered liquors should be made by following all the precautions necessary to secure accuracy with unbuffered solutions. This is also important in beet sugar manufacture where pH control is used extensively on the pan liquors. The type of results which may be expected on such liquors is shown in Table VI.

Table VI—Determination of pH of Purified Sugar Solutions

Sample	Short-Range Indicators	Wide-Range Indicator with pH of: 5.25	7.45	9.10	Max. variation
	pH	*pH*	*pH*	*pH*	*pH*
1	6.5	6.0	6.8	7.2	1.2
2	7.3	7.2	7.6	8.2	1.0
3	6.5	6.0	6.6	7.2	1.2
4	5.8	5.4	5.8	6.2	0.8

Effect of Diluting Buffered Solutions—In order to study the effect of dilution observed by Fawcett and Acree on the pH readings secured with a wide-range indicator at variable reactions, several well-buffered solutions were diluted with distilled water (pH 5.8) and the pH values determined as before. The buffer solutions used were 0.05 *M* potassium acid phthalate, a 0.05 *M* phosphate mixture, and 1.0 per cent solutions of sodium bicarbonate and sodium sesquicarbonate. The results are shown in Tables VII, VIII, IX, and X.

Table VII—Effect of Diluting Potassium Acid Phthalate Solution

Sample	Dilution	Short-Range Indicators	Wide-Range Indicator with pH of: 5.25	7.45	9.10	Max. variation
		pH	*pH*	*pH*	*pH*	*pH*
1	None	4.0	4.0	4.0	4.0	0.0
2	1:10	4.0	4.2	4.4	4.6	0.4
3	1:100	4.3	4.6	4.8	5.2	0.6
4	1:1000	4.8	5.0	5.8	6.6	1.6
5	1:10000	4.8	5.2	6.4	7.4	2.2

Table VIII—Effect of Diluting Phosphate Buffer Solution

Sample	Dilution	Short-Range Indicators	Wide-Range Indicator with pH of: 5.25	7.45	9.10	Max. variation
		pH	*pH*	*pH*	*pH*	*pH*
1	None	6.9	7.0	7.0	7.0	0.0
2	1:10	6.9	7.0	7.0	7.0	0.0
3	1:100	6.7	6.4	6.8	7.0	0.6
4	1:1000	6.5	6.2	6.8	8.0	1.8
5	1:10000	6.4	5.2	6.8	8.6	3.4

Table IX—Effect of Diluting Sodium Bicarbonate Solution

Sample	Dilution	Short-Range Indicators	Wide-Range Indicator with pH of: 5.25	7.45	9.10	Max. variation
		pH	*pH*	*pH*	*pH*	*pH*
1	None	8.2	8.2	8.2	8.3	0.1
2	1:10	8.2	8.2	8.2	8.4	0.2
3	1:100	7.6	7.0	7.6	8.2	1.2
4	1:1000	6.6	6.4	6.8	8.0	1.6
5	1:10000	6.1	5.6	6.4	7.8	2.2

Table X—Effect of Diluting Sodium Sesquicarbonate Solution

Sample	Dilution	Short-Range Indicators	Wide-Range Indicator with pH of: 5.25	7.45	9.10	Max. variation
		pH	*pH*	*pH*	*pH*	*pH*
1	None	10.2	10.2	10.2	10.2	0.0
2	1:10	10.2	10.2	10.2	10.2	0.0
3	1:100	9.7	9.0	9.2	9.6	0.6
4	1:1000	8.4	6.4	7.0	8.6	2.2
5	1:10000	6.4	5.4	6.6	8.4	3.0

Summary of Results

The readings given in the tables tend to show the magnitude of the errors that may be encountered when attempts are made to determine the pH of many practical solutions with a single wide-range indicator.

It is apparent that so-called universal or utility indicators covering a wide pH range can be used with safety only on well-buffered materials. Unfortunately in testing solutions of unknown nature, there is no simple or rapid way of determining the buffer capacity. Consequently, pH control under such circumstances becomes somewhat uncertain. There being no way of checking results, the operator may make serious errors.

In order to avoid the effect of variation in pH between the indicator and the unknown solution, a number of different solutions of the wide-range indicator might be adjusted in steps of 1.0 between pH 3.0 and 11.0. By application of the isohydric-indicator technic with these nine indicator solutions, it is possible to determine the pH of weakly buffered solutions with a fair degree of accuracy. Three wide-range indicator solutions adjusted at pH 3.0, 7.0, and 11.0 can be used for preliminary field or factory tests. Intermediate pH adjustments of the indicator can be made up by using different calculated ratios of drops of the pH 3.0, 7.0, and 11.0 solutions for the final tests. For more accurate work, however, such a procedure offers no advantage over the use of several short-range indicators, with the disadvantage that a mixed indicator is rarely so sensitive as several indicators used separately because the color changes are not so distinct.

Since single-test unadjusted wide-range indicators may yield such erroneous results with slightly buffered materials, this practically prohibits their use in many fields. It is unfortunate that the use of such unadjusted indicators has been encouraged because it may not only cause economic loss but may make the user lose confidence in pH control.

Literature Cited

(1) Birge and Acree, *J. Am. Chem. Soc.*, **41**, 1037, footnote (1919).
(2) Clark, "The Determination of Hydrogen Ions," 3rd ed., pp. 96–98, Williams & Wilkins, 1928.
(3) Fawcett and Acree, *J. Bact.*, **17**, 163 (1929); Ind. Eng. Chem., Anal. Ed., **2**, 78 (1930).
(4) Karracker, *Soil Science*, **15**, 473 (1923).
(5) Marsh, *Science*, **59**, 216 (1924).
(6) McCrumb and Kenny, *J. Soc. Chem. Ind.*, **49**, 425T, 427T (1930).
(7) Pierre and Fudge, *J. Am. Chem. Soc.*, **50**, 1254 (1928).
(8) Schlegel and Steuber, Ind. Eng. Chem., **19**, 631 (1927).
(9) Wehmhoff, U. S. Govt. Printing Office Repts., *Tech. Bull.* **8** (1930); *Ibid.*, **11** (1930).

New Autographic Machine for Testing Tensile Properties of Rubber[1]

George J. Albertoni

Research Laboratories, Goodyear Tire & Rubber Co., Akron, Ohio

A description is given of a testing machine for the measurement of the tensile strength of materials having considerable deformation, such as rubber.

A stress-strain recording device is described in which the strain recorded responds to the separation between a pair of independently movable pointers which may be made to follow the separation of two marks, spaced upon the sample before insertion in the machine.

Mechanical means are also described to correct for variations in the test-piece cross section, and to produce equal chart displacements for equal angular deviations of the inclination balance.

MACHINES have been devised heretofore for determining the per cent elongation of rubber with application of load, but such machines are open to criticism because of calculations required and the personal error involved in determining the elongation.

Identified with this subject, as recorded in the literature, we find such names as Breuil, 1907 (*2*), Schopper and Dalen, 1909 (*8*), Beadle and Stevens, 1909 (*1*), Schwartz, 1910 (*9*), Olsen, 1910 (*6*), Cheneveau and Heim, 1912 (*4*), Scott, Cooey, and Burkley, 1922 (*3*), Depew, 1922 (*5*), Schob, 1923 (*7*), and Williams, 1925 (*10*).

The machine herein described, as designed by the author, aims to avoid the criticisms above mentioned by embodying a recording device so operated as to provide mechanically a stress-strain curve upon ordinary coördinate paper, giving the desired results in a form which can be directly used for record.

Referring to the photographs and sketches, Figure 1 represents a general view of the machine and illustrates with some detail the following parts: *L*, pendulum-lifting arrangement; *S*, scales on which are directly indicated the settings of the weight lifter for the different gages of the test pieces; *A*, arcuated member to which is trained the cord connecting the pendulum displacement with the horizontally moving plate of the charting arrangement.

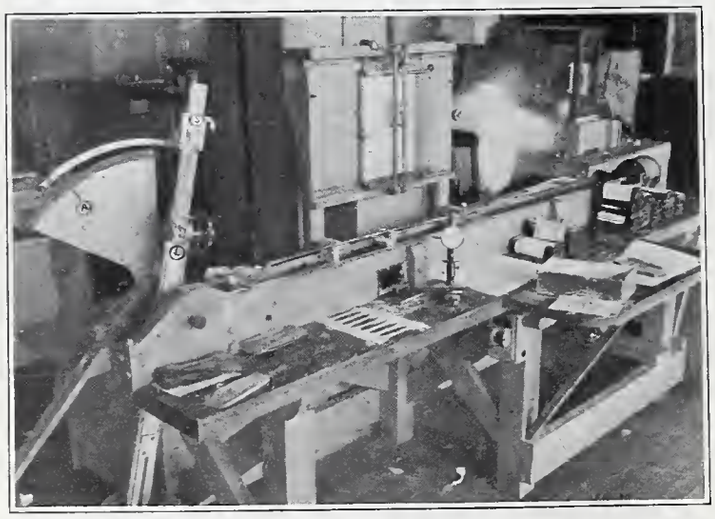


Figure 1—General View of Machine

This photograph shows a general view of the machine as in use at the different Goodyear plants.

A favorable comparison with any other standard machine is obtained when the following features are considered: (1) the comparatively high speed of performance (25 tests and more per hour); (2) the accuracy of results; (3) the duplicability obtained by mechanical means in preference to visual observation.

No calculations are required and the records obtained can be used directly for the measurement of the area under the stress-strain curve or for any other purpose.

Figure 2 is intended to illustrate the following devices: *C*, the type of clamps used to hold the test piece in position; *R*, the alignment rollers used to counteract the tendency of the rubber to slip from the clamps on account of the lifting action of the pointers of the two elongation carriages; *F*, the two followers or carriages following the two bench marks at the reduced portion of the test piece; *D*, the type of device used to engage or disengage the clamp carriage at the right, from the rotating driving screw; *W*, the method of driving the chart-supporting plate by means of a counterbalancing weight, in response to the pendulum movement; and *P* the type of pen support and the guides along which the small pen carriage is raised or lowered by the lengthening or shortening of the distance between the two carriages following the two bench marks.

Figure 3 represents diagrammatically the fundamental principles on which the performance of the machine is based. The sketch also illustrates the linking of the different parts and the coördination of the movement of the chart with the movement of the pen, to produce the curve representing the stress-strain relationship. As indicated at the left, the force-measuring device is a modified pendulum balance. The weights operate in a slot and can be raised or lowered to decrease or to increase the length of the operating arm. At the center of the pendulum, secured to the shaft, is illustrated the type of cam used to maintain such a rate of loading as to produce, on the chart, equal spacing for equal angular devia-

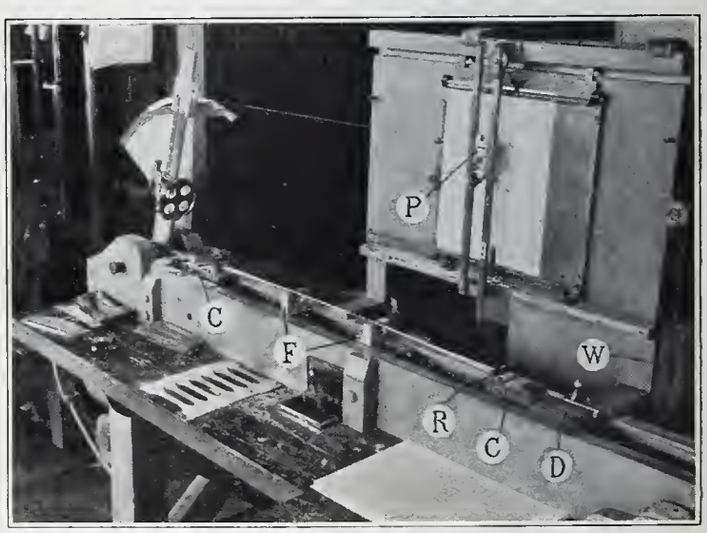


Figure 2—Machine with Test Piece in Place

[1] Received November 15, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

tions of the pendulum. At the center of the sketch is shown the method of recording the load and the method of transmitting to the recording pen the separation between marks. A slight tension of the cord interconnecting the movable members of the elongation system is effected by the small weight of the pen carriage. The method of obtaining the vertical line expressing the ultimate load is also obtained by the indirect action of the weight of the pen carriage. In fact, this will drive together the two followers as soon as the test piece breaks, and therefore as soon as the points of the two followers are released from their hold against the rubber sample.

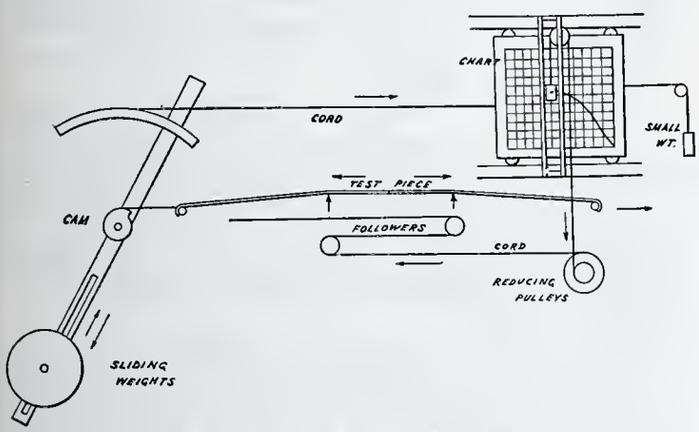


Figure 3—Diagram of Machine

Figure 4 shows on the same chart the stress-strain curves obtained by three typical factory stocks: a tread stock, a carcass stock, and a truck-tube stock. In this chart the load is expressed in pounds per square inch. The curves are, however, generally recorded in charts expressing the load in kilograms per square centimeter. The two types of charts are so designed as to make the readings interchangeable. As shown in Figure 4, the straight lines parallel to the elongation axis determine with the load axis the ultimate load of the test pieces.

Figure 5 represents a somewhat more detailed view of the machine. The sketch is somewhat schematic, the purpose being to emphasize the interconnection of the different moving members. The front rail is removed so as to show the clamp carriages, the construction of the followers, the method of operation of the small pulleys supported by the followers, the reducing pulleys, and other important parts.

Method of Recording Stress-Strain Data

In the following is outlined a detailed description of the most important parts of the machine, and their performance in coördination with each other, to produce the stress-strain curve.

Weighing Mechanism—A lever, 1 (Figure 5), is pivotally mounted upon one end of the table 2, adjacent to the carriage guides, 3 and 4 (Figure 8). The lever (Figures 6 and 7) is constructed of a top portion, 5, provided with a rack, and a lower portion, 6, having an elongated slot whereby a weight or set of weights can be secured at different positions on the lower part of the lever. In order to have means for maintaining the lever in position advanced from the vertical, it is provided with pawls mounted upon its lower end, 8. The pawls are normally engaged with a rack, 9 (Figure 5), secured to the table, but means are provided for holding the pawls out of engagement whenever required.

A bracket, 10 (Figure 7), is secured to the lever and supports an arcuated grooved member, 11 (Figure 6). To this arcuated member is trained a cord, 12 (Figure 5), transmitting the motion of the weighing device to the recording mechanism.

Compensation for Gage Variations of Test Pieces—In order to obtain an accurate comparison between different test pieces of the same width but of different gage, the adjusting device, 13, is utilized. This device is raised or lowered by first raising the pin, 14, at the end of the lever, 15, from engagement with the wheel, 16, perforated at the edge, and then by turning the knurled wheel, 17, to operate the rack and pinion, 18 and 19. The adjusting device is rigidly connected by means of two lateral bridles to a cross-shaped piece supporting the weights, 7. By this arrangement it is possible to raise or lower the pendulum weights with small effort and with rapidity in setting.

It is obviously possible to take care of practically any reasonable variation of gage, the only limitations being an excessive weight or an excessive length of moment arm. In the latest machines use is made of three sets of weights, making possible the testing of samples in a range of thicknesses from 0.95 to 3.40 mm.

There are three scales, each related to one of the three sets of weights, and to a definite group of gage variations. The gage of the test piece is indicated in the corresponding scale, and to these positions is lifted or lowered the weight-lifting device, 13.

Cam Member—The cam member, 20, is mounted upon the pendulum lever to serve as a connection, together with a steel ribbon or a small sprocket chain, to one of the two carriages to which the test piece is clamped. The cam member is designed according to a curve calculated to compensate for the proportionally decreasing acting leverage of the pendulum weight with the increase of the pendulum displacement. In calculating the cam shape, account is also taken of the action of the counterbalance weight, 28.

As the pendulum lever, 6, is displaced from the vertical, the moment arm of the test piece is continuously changed so that the load is in every instance proportional to the distance traversed by any point of the arcuated member, 11. Equal increments of load are therefore made directly proportional to equal angular displacements of the pendulum from the vertical.

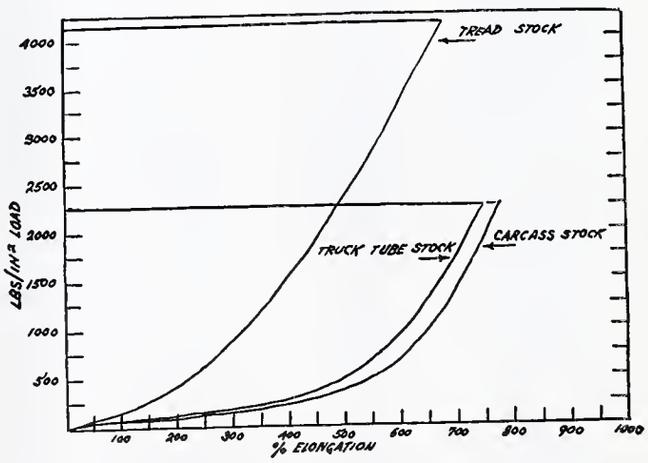


Figure 4—Stress-Strain Curves Obtained with Three Factory Stocks

Charting Load—A recording device is mounted upon a frame, 21, which is supported by the guide member, 3. A plate, 22, is mounted upon a number of rollers, 23, which ride in channels of the frame. A cord, 12, is connected at one end, by means of a small regulating drum, 24, to the plate, trained over the grooved member, 11, and connected thereto by means of an adjustable thumb screw, 25. Another cord, 26, connected to the moving plate, is trained over a pulley, 27, mounted upon the frame, and is secured to a weight, 28, by the other end. Two guides, 29, are mounted upon the frame to provide a support for a member, 30, that carries a tracing

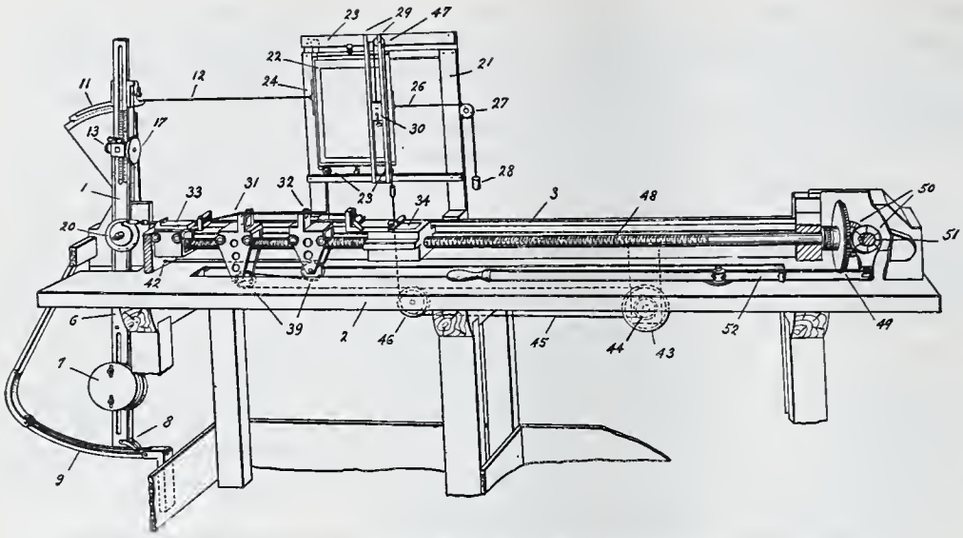


Figure 5—Sketch of Machine Emphasizing Interconnection of Moving Members

pen. The pen may be moved into and out of contact with the plate, and therefore with the coördinate paper mounted thereon.

Charting Elongation—The most important parts of the elongation charting system are the elongation carriages, 31 and 32 (Figures 5 and 8), operating between the carriage, 33, and the sliding member, 34, which are supporting the clamping devices at the two ends of the test piece. These members, 31 and 32, are similar in construction, each having rollers mounted upon the sides and so adjusted as to ride in the channels, 36, of the guides. They also have two lower arms, 37 (Figure 9), which carry a shaft, 38, upon which a pulley, 39, is freely mounted. A V-shaped member, 40, is mounted in a recess in the top of both members, supporting a centrally located pointer, 41. These pointers have a shank set within a spring and exert a slight pressure on the test piece.

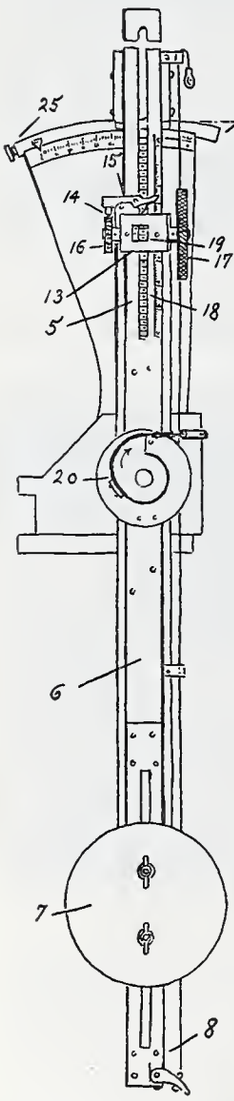


Figure 6—Front View of Weighing Mechanism

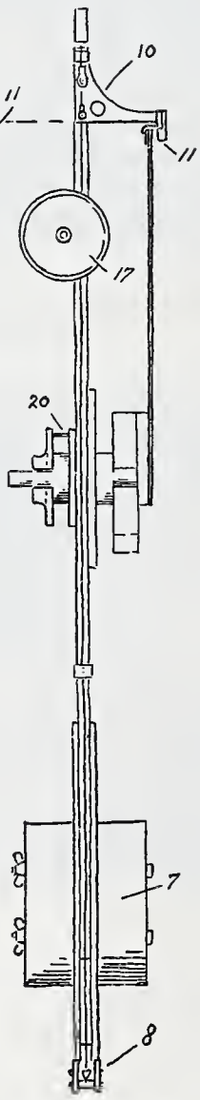


Figure 7—Side View of Weighing Mechanism

The two members 31 and 32 differ in construction in that the arms of the member 31 are somewhat longer than those of the member 32, in order to stagger the pulleys with respect to each other. The members 31 and 32 are connected together and are interconnected to the member 30 by means of a system of two cords.

A cord secured at the left end to the table, 42, is trained first over the pulley of the follower 32 at the right, next over the one of the follower at the left, 31, then wrapped once or twice over the largest of the two reducing pulleys, 43. A second cord, 45, first secured and wrapped once over the smallest of the two reducing pulleys, 44, is trained over a pulley, 46, mounted upon the table, 2, then over the small idler at top of the pen-carriage guides, and finally is fastened to the pen carriage. The two pulleys 43 and 44 are utilized to provide a reduction system, so as to secure proper length of movement of the member 30 with respect to the separation of the carriages 31 and 32.

Straining Mechanism—This mechanism, as represented in Figure 5, illustrates the original type constructed, which was designed both for tensile tests and for the study of the hysteresis of rubber compounds. In the machine as illustrated in Figures 1 and 2, the straining mechanism is simplified and designed to provide only one direction of motion.

The mechanism, as represented in Figure 5, consists of a number of movable members mounted between two guides, of which only the rear one, 3, is shown. A longitudinally extending threaded shaft, 48, is mounted between the two guide members and is driven through the agency of a bevel gear, 49, mounted upon one end. This gear is driven by

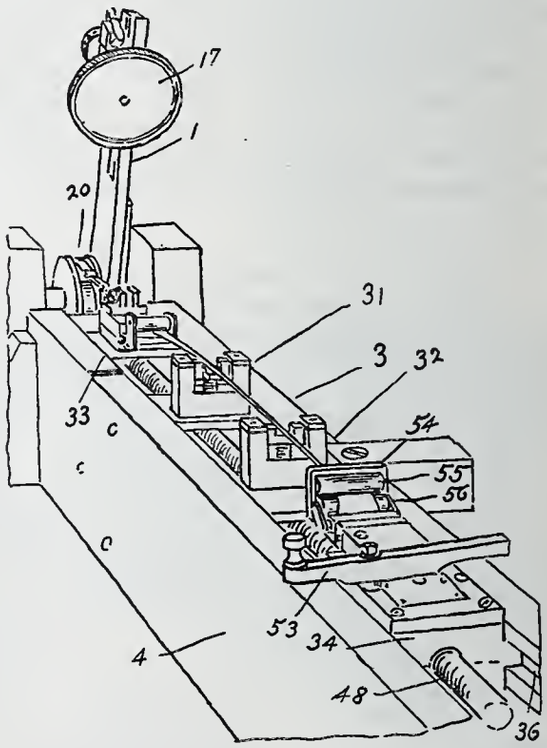


Figure 8—Diagram Showing Test Piece in Position

pinions, 50, mounted on a shaft connected to a lever, 52, whereby these pinions may be moved into and out of engagement. Any suitable means may be employed for driving the shaft, 51, such as a motor belted to it. A carriage, 34, is mounted upon the shaft (Figure 8), having an internally threaded portion adapted for engagement with the threaded shaft or disengagement by means of a lever, 53, mounted upon the carriage. The carriage is provided with flanges to fit into the channels of the guides. To the carriage is attached a clamping device including a yoke, 54, which carries a

roller, 55, coöperating with the roller 56, to secure the test piece to the carriage. The speed of jaw separation used for testing is 30 inches per minute, but provision is made to operate at 20 inches per minute whenever required.

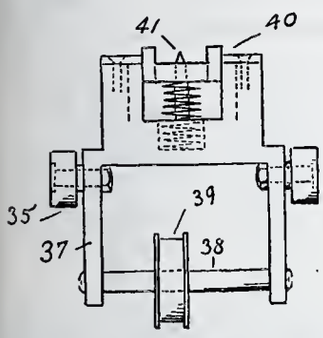


Figure 9—Diagram of Follower Mechanism

Operation of Machine

The operation of the machine is apparent from the preceding description.

The type of test piece used is the ordinary dumbbell, 1 cm. being the width of the reduced portion. Marks at a definite distance are made on the narrower part.

The test piece is secured at one end to the clamping device of the carriages, 33 (Figures 5 and 8), attached to the inclination balance. Bridging over the pointers of the elongation carriages, the other end is clamped to the sliding member 34. The plate is adjusted by means of the small drum in such a position that the tracing device moves on the ordinate, passing through the value zero of the abscissa, when the pendulum is in the vertical position. The carriages 31 and 32, drawn in contact by the weight of the member 30, are dimensioned in such a way that the corresponding pointers are at the same distance as the distance between marks. During the initial elongation of the test piece these pointers are set to correspond with the marks, no further attention being required after the first few inches of stretch. Further, since the carriages 31 and 32 follow the separation of the marks, the tracing pen moves proportionally along the ordinates of the coördinate paper.

In reference to the load, when the pendulum lever is moved in response to the stretching of the test piece, the weight is permitted to draw the plate along its support, whereby normal movement of the plate with respect to the tracing device results. A curve is thus traced which provides a record showing the relation between the load imposed and the resulting elongation.

Acknowledgment

The author desires to express his appreciation for the valuable suggestions and criticism offered by W. W. Vogt during the development of the machine.

Literature Cited

(1) Beadle and Stevens, *J. Soc. Chem. Ind.*, **28**, 1111 (1909).
(2) Breuil, *Caoutchouc & gutta-percha*, **4** (1907); "India Rubber and Gutta-percha," pp. 250–257, Scott, Greenwood, 1910.
(3) Burkley, *India Rubber World*, **67**, 24 (1922).
(4) Cheneveau and Heim, *J. phys.*, **2** (5), 535–50 (1912); *Caoutchouc & gutta-percha*, **11**, 8429–8432 (1914).
(5) Depew, *India Rubber World*, **67**, 154 (1922).
(6) Olsen, *Proc. Am. Soc. Testing Materials*, **10**, 588–91 (1910).
(7) Schob, *Gummi-Ztg.*, **37**, 235 (1923).
(8) Schopper and Dalen, "Lectures on India Rubber," pp. 289–293 (1908).
(9) Schwartz, *J. Inst. Elec. Eng.*, **44**, 693–752 (1910).
(10) Williams, *India Rubber World*, **72**, 411 (1925).

Accurate and Adaptable Micro-Kjeldahl Method of Nitrogen Determination[1]

W. F. Allen

Kedzie Chemical Laboratory, Michigan State College, East Lansing, Mich.

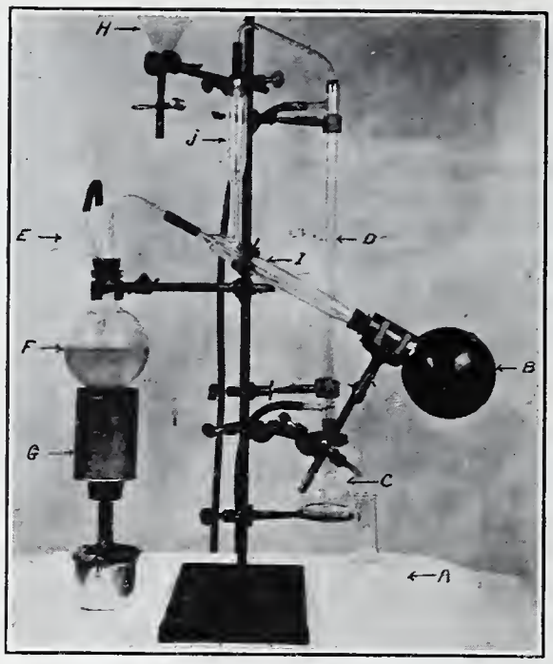
THE demand for an accurate, simple, and adaptable method for the micro-determination of nitrogen to be used in connection with caffeine analysis of decaffeinated coffee resulted in the development of the apparatus shown here. It is essentially a micro-Kjeldahl distillation apparatus similar to those of Pregl's, and Parnas and Wagner's (*2*). However, it was found to be easier to operate and capable of handling larger samples than the latter. The use of rubber connections was not eliminated, as was accomplished in the apparatus perfected by Kemmerer and Hallett (*1*), but the apparatus gave very accurate results, and was found to be easily constructed by anyone capable of doing simple glass blowing.

The entire apparatus was made of Pyrex glass. Parts *I* (23.5 cm. long) and *J* (21.0 cm. long) were made from 25 × 200 mm. test tubes. The inside condenser tubing extending over to the top of the safety trap *J* was made of 9-mm. tubing. The condenser is 60 cm. in length.

The method of procedure is as follows: The sample was digested in the 250-cc. Florence flask *A*. This size flask was found capable of handling samples requiring not over 10 cc. of concentrated sulfuric acid in the digestion mixture. With samples containing a large amount of organic matter, it was found to be very convenient to add a few drops of 30 per cent hydrogen peroxide during the last part of the digestion. The cooled digested sample was then diluted with freshly boiled distilled water, care being taken that the flask was not over one-fourth full. The flask was placed in the asbestos-lined jacket *B* and clamped into position as shown. The jacket eliminated the use of a second burner by keeping condensation of steam down to a minimum. However, very satisfactory results were obtained without the use of the jacket by applying heat to flask *A* only during the last 3 or 4 minutes of the distillation.

For samples containing up to 20 mg. of nitrogen, 15 cc. of 4 per cent boric acid (*3*) and 15 drops of 0.02 per cent methyl red indicator were measured into the 150-cc. evolution flask *C*, which was then placed in position under the condenser *D* with a wide cork resting on top of the flask. Freshly boiled distilled water was next added through funnel *E* into the 500-cc. balloon flask *F* used as a steam generator. Heat was applied to flask *F* by a Bunsen burner *G*, having a shield around the top to prevent air currents from causing variation in the amount of heat applied. Immediately after starting to heat the steam generator, a slight excess of concentrated sodium hydroxide was added through funnel *H* and then washed down with a few cubic centimeters of water. This funnel was immediately closed with a pinch clamp. Distillation was continued at such a rate that no bubbling of steam occurred in the receiving flask *C*. After about 125 cc. of liquid had distilled over, in about 12 minutes, the receiving flask was lowered so that the tip of the condenser was about 2 cm. above the surface, and the tip washed down with a small stream of water. Distillation was continued at an increased rate for one minute longer. The pinch clamp on funnel *H* was then released before removing the steam generator to prevent suction. A blank was always run using the same

[1] Received January 20, 1931.



Apparatus for Micro-Kjeldahl Method

reagents and procedure as with the samples, after the apparatus had been thoroughly steamed for at least 15 minutes. Care was taken that the same amount of liquid was contained in each flask to insure the same intensity of color. The contents of the receiving flask *C* from a sample were titrated directly with dilute standard sulfuric acid from a microburet; and the end point was taken when the shade of color of the indicator exactly matched that of the blank. This proved to be a very faint pink at a pH of about 5.7. By matching the blank it was unnecessary to subtract a blank correction from the amount of acid used.

Table I—Comparative Accuracy of Micro-Kjeldahl Method

Samples Analyzed	Nitrogen in Sample	Error with Macro-Kjeldahl	Error with Micro-Kjeldahl
	Mg.	%	%
8	21.114	0.62	0.29
6	1.000		1.20
4	0.583	1.85	0.24
4	0.100		3.00

It can be readily observed that this apparatus and procedure can be used with rapidity and accuracy on samples requiring as much as 10 cc. of concentrated sulfuric acid in the digestion mixture, as well as samples containing as little as 0.1 mg. of nitrogen. The comparative accuracy of this method with the macro-Kjeldahl method is shown in Table I. By running two sets of apparatus at the same time it was found that 20 samples could easily be analyzed in a half day.

Literature Cited

(1) Kemmerer and Hallett, Ind. Eng. Chem., **19**, 1295 (1927).
(2) Pregl, "Quantitative Organic Microanalysis," pp. 94–104, Blakiston, 1924.
(3) Scales and Harrison, J. Ind. Eng. Chem., **12**, 350 (1920).

Use of Boric Acid in Micro-Kjeldahl Determination of Nitrogen[1]

Norman M. Stover and Reuben B. Sandin

Department of Chemistry, University of Alberta, Edmonton, Alberta

The use of boric acid in absorbing ammonia in nitrogen determinations by Pregl's micro-Kjeldahl method has been found to give accurate results.

The distillate containing the ammonia does not need to be boiled before titrating.

A mixed indicator containing methyl red and tetrabromophenol blue has been found to give good results in boric acid solution.

The use of a saturated solution of boric acid in place of a standard acid to absorb ammonia in nitrogen determinations by the Kjeldahl method has been reported a number of times. It was first proposed by Winkler (*8*), has been mentioned by Scales and Harrison (*6*), and recommended by Spears (*7*). The authors (*5*) have also used boric acid to absorb ammonia in the determination of organic nitrogen in liquids by an alkaline fusion method.

The use of boric acid in nitrogen determinations is based on the principle that ammonia is absorbed by the weak boric acid and is titrated in this solution with a strong acid, such as sulfuric or hydrochloric. Ammonium borate is probably formed, and in the presence of a strong acid the ammonia is again released to form the salt of the strong acid.

The fact that boric acid gives results almost identical with those obtained when using a standard acid has led the authors to determine the possibility of using it in the micro-Kjeldahl method as outlined by Pregl (*4*). It has several advantages, as stated by Scales and Harrison (*6*), and also a few other small points in its favor. A minimum amount of the only standard solution (standard acid) required is used. There is no back titration as the ammonia in the boric acid is titrated directly, and thus a saving is made in the use of standard reagents. Also, it is considered by some to be easier to prepare a standard acid solution than a standard alkali solution, and a carefully standardized acid solution is less subject to change in storage.

Experimental Procedure

Attempts were made to find a suitable indicator for use in boric acid solution when absorbing small amounts of ammonia. The following indicators were tried: bromophenol blue (0.1 gram in 3 cc. of 0.05 *N* sodium hydroxide and diluted to 250 cc.), tetrabromophenol blue (0.1 gram in 20 cc. of warm alcohol and diluted to 100 cc.), sodium alizarin sulfonate (1 per cent in water), methyl red (0.1 per cent in 95 per cent alcohol), a mixed indicator containing methyl red and methylene blue (0.1250 gram of methyl red and 0.0825 gram of methylene blue in 100 cc. of 90 per cent alcohol), and a mixture of methyl red and tetrabromophenol blue (made by mixing equal volumes of solutions of the separate indicators). The mixed indicator containing methyl red and methylene blue has been recommended by Johnson and Green (*3*). The new indicator, tetrabromophenol blue,[2] was developed recently by Harden

[1] Received January 30, 1931.

[2] W. C. Harden of the laboratories of Hynson, Westcott, and Dunning kindly supplied the sample of this indicator.

and Drake (*2*). This name for the indicator has been suggested by Kolthoff as a trade name, the proper name for the compound being tetrabromophenol-tetrabromosulfonephthalein.

Since Scales and Harrison (*6*) obtained good results with bromophenol blue when used in the ordinary Kjeldahl method, and the authors (*5*) likewise found this indicator satisfactory when used in their alkaline fusion method, it was thought the same indicator might be used in the present investigation. Preliminary trials indicated, however, that bromophenol blue possesses a sufficient salt error to render the indicator useless in boric acid solution when titrating small amounts of ammonia. This is readily shown by the effect of varying amounts of ammonium sulfate on the color of the indicator in boric acid solution. Also, when using $N/70$ hydrochloric acid for titrating the ammonia, the end point is not sharp.

With the other indicators, no salt error was noticeable. This was determined for each indicator by adding 2 drops of the indicator (4 drops in the case of the mixed indicator containing methyl red and tetrabromophenol blue) to each of three solutions containing 2 cc. of 4 per cent boric acid, varying amounts of ammonium sulfate solution (furnishing, respectively, 0.5 mg., 1 mg., and 2 mg. of nitrogen), and enough freshly boiled, cooled, distilled water to make 50 cc. Each indicator or mixture of indicators showed its characteristic color regardless of the concentration of ammonium sulfate present, thus showing the absence of any salt error. The colors shown were as follows: tetrabromophenol blue, pale blue; sodium alizarin sulfonate, yellow; methyl red, faint pink; mixture of methyl red and methylene blue, bluish green; mixture of methyl red and tetrabromophenol blue, pale gray-violet.

The effect of varying amounts of boric acid on the indicators was also determined. This was done by adding 2 drops of the indicator (4 drops in the case of the mixed indicator containing methyl red and tetrabromophenol blue) to each of two solutions containing, respectively, 2 cc. of 4 per cent boric acid and 5 cc. of 4 per cent boric acid and enough freshly boiled, cooled, distilled water in each case to make 50 cc. of solution. Tetrabromophenol blue showed no difference in color in the two solutions. With increasing concentration of boric acid, sodium alizarin sulfonate changed to a lighter yellow, methyl red to a deeper pink, mixed methyl red and methylene blue from bluish green to pure blue, while mixed methyl red and tetrabromophenol blue took on a reddish tint. Hence most of the indicators were affected by increasing concentrations of boric acid.

In the case of tetrabromophenol blue, further work showed that the end point is difficult to determine when using $N/70$ hydrochloric acid to titrate the ammonia held by boric acid solution, as the color of the indicator in boric acid solution containing absorbed ammonia is only a somewhat deeper blue than a control solution containing the same amount of boric acid and ammonium sulfate equivalent to 1 mg. of nitrogen. It should be mentioned that the color changes shown by tetrabromophenol blue are the same as those shown by bromophenol blue. The color change of sodium alizarin sulfonate is from yellow in acid solution to violet in alkaline solution. Yet when small amounts of ammonia were distilled into a boric acid solution, this indicator underwent a color change only from yellow to a deeper golden yellow instead of to a violet color. Hence the two indicators, tetrabromophenol blue and sodium alizarin sulfonate, were found to be unsuitable.

The other three indicators proved more satisfactory. Their practical value was determined as follows: A solution of ammonium sulfate was made so that 5 cc. contained approximately 1 mg. of nitrogen. A definite volume of this solution, measured from a buret, was introduced into the micro-Kjeldahl distillation apparatus, an excess of saturated sodium hydroxide solution added, and the ammonia distilled off, using Pregl's method of steam distillation as modified by Clark and Collip (*1*). In one series, the ammonia was determined by the usual micro method—i. e., absorbing the ammonia in an excess of $N/70$ acid and titrating the excess acid with approximately $N/70$ carbonate-free sodium hydroxide solution (the relationship between the acid and alkali being known). In this series, methyl red was used as indicator, the acid solution being boiled for about 1 minute and then cooled just before titrating with the $N/70$ alkali. In other series, the ammonia was absorbed in a solution containing 2 cc. of 4 per cent boric acid solution, 2 cc. of distilled water, and 2 drops of indicator. The distillates (about 50 cc. in each case) were titrated at once with $N/70$ hydrochloric acid until the color of the solution matched that of a control containing 2 cc. of 4 per cent boric acid solution, 5 cc. of ammonium sulfate solution (1 mg. of nitrogen), 2 drops of indicator, and boiled distilled water to 50 cc. The control is necessary because, as already shown, the colors of the indicators vary with different concentrations of boric acid. The amounts of nitrogen recovered from the original ammonium sulfate solution in each series were calculated (1 cc. of $N/70$ HCl = 0.2 mg. of nitrogen). By comparing these amounts it was possible to ascertain whether the boric acid method gave as good results as the ordinary method and also which indicator was most suitable. Some typical results are given in the first column of figures in Table I.

Table I—Comparison of Results with Two Methods

Sample	Indicator	Nitrogen Recovered from Ammonium Sulfate Solns.	Nitrogen Recovered from Same Sample of Urine
		Mg.	*Mg.*
		ORDINARY METHOD	
1	Methyl red	0.507	0.575
		0.509	0.585
		0.509	0.573
		0.509	Av. 0.578
2		1.005	
		1.005	
		1.005	
		1.007	
		BORIC ACID METHOD	
1	Methyl red	0.504	0.565
		0.505	0.562
		0.505	0.575
			Av. 0.567
2		1.002	
		1.002	
		1.004	
1	Methyl red and methylene blue	0.505	0.575
		0.505	0.575
		0.505	0.570
			Av. 0.573
2		1.005	
		1.005	
		1.005	
1	Methyl red and tetrabromophenol blue	0.502	0.575
		0.505	0.578
		0.506	0.584
			Av. 0.579
2		1.005	
		1.005	
		1.006	

Finally, the indicators were used in the determination of nitrogen in urine by both the ordinary micro-Kjeldahl method and the authors' boric acid method. The procedure used was to dilute 5 cc. of urine to 100 cc., and then digest 1 cc. of the diluted urine with concentrated sulfuric acid, copper sulfate, and potassium sulfate as directed by Pregl (*4*). After digestion, the contents of the digestion flask were cooled and

transferred to the distillation apparatus and distilled as before, except that a small amount of sodium thiosulfate solution was added with the saturated sodium hydroxide solution to precipitate the copper, and 3 drops of Nujol to prevent frothing. Nujol was found to be better than amyl alcohol in that it did not boil off. Typical results are shown in the last column of figures in Table I.

It will be observed that with the use of boric acid and the mixed indicator containing methyl red and tetrabromophenol blue, results were obtained which were very close to those obtained by the ordinary method. It was also found that this mixed indicator gave a sharp end point, the color changing from a clear green in alkaline solution to a gray color at almost the end point, and then to a pale gray-violet with slightly more acid.

Scales and Harrison (*6*) found that 50 cc. of 4 per cent boric acid solution would recover 95 mg. of nitrogen as ammonia with accuracy. Hence, 2 cc. of a 4 per cent solution would be quite sufficient when using the micro-Kjeldahl method for the determination of nitrogen in urine. Also, instead of diluting 2 cc. of a 4 per cent solution with 2 cc. of distilled water, 4 cc. of a 2 per cent solution could be used directly.

Literature Cited

(1) Clark and Collip, *J. Biol. Chem.*, **67**, 621 (1926).
(2) Harden and Drake, *J. Am. Chem. Soc.*, **51**, 562, 2278 (1929).
(3) Johnson and Green, Ind. Eng. Chem., Anal. Ed., **2**, 2 (1930).
(4) Pregl, "Quantitative Organic Microanalysis," Blakiston, 1924.
(5) Sandin and Stover, *Can. J. Res.*, **2**, 264 (1930).
(6) Scales and Harrison, Ind. Eng. Chem., **12**, 350 (1920).
(7) Spears, *J. Assocn. Official Agr. Chem.*, **5**, 105 (1921).
(8) Winkler, *Z. angew. Chem.*, **26**, 231 (1913).

An Easy Method of Marking Chemical Glassware[1]

K. H. Morkert and W. D. Hatfield

Sanitary District, Decatur, Ill.

ETCHING glassware in the ordinary routine laboratory with hydrofluoric acid is not an easy task, consequently labeling of flasks, bottles, and rough calibrations is usually done with gummed labels, sometimes covered with a wax coating, or with colored wax pencils. These labels are not permanent, particularly with articles which must be washed regularly.

For some time the stoppers and the bottles, as well as the capacities of the bottles when stoppered, used for incubation of the dilutions for determination of the biochemical oxygen demand have been numbered in this laboratory. The use of these calibrated bottles greatly decreases the routine for setting up and later titrating the B. O. D.'s. The scratching of numbers and letters on the stoppers and bottles with a glass marking pencil is a hard and tedious job and cannot be done neatly.

A merchant stuck pennants on his plate glass windows with water glass, and when he removed the pennants he found his plate glass etched so permanently that he could not wash the etching off with acid, alkali, or abrasives. His call for help aroused the interest of the authors in this problem.

It occurred to the authors that a permanent etching might easily be obtained by writing the letters and numbers on glassware using water glass and a steel pen. The results have been very satisfactory and, so far as is known, this method of marking chemical glassware is not commonly used. The technic is summarized as follows:

Reagent

Water glass as purchased from a drug store is 40 per cent sodium silicate. This solution is a little too thick for easy application with a steel pen. A 30 per cent solution obtained by diluting 75 cc. of the 40 per cent solution to 100 cc. with distilled water gives a solution of the proper consistency. One hundred cubic centimeters will mark a large number of bottles. Care should be taken to rinse out glassware used in measuring and diluting the reagent. The reagent may be kept in an ordinary bottle with a rubber stopper.

A common steel pen is used to apply the reagent to the glassware.

Marking of Pyrex and Resistance Glass

The article to be marked should be cleaned and thoroughly dried. Dip the pen in the sodium silicate solution, drain the excess reagent from the pen point by touching the pen to the mouth of the reagent bottle, and mark the desired letters or numbers on the glass. A few experimental markings will show the amount of reagent and the best pressure on the pen for the desired results. Allow the markings to dry for a few minutes and then go over them with a second application. This will leave a colorless marking raised about 1 mm. above the glass surface. Where there are a number of articles to be marked, the pen must be washed frequently to prevent the reagent from crystallizing on the pen point.

After the applications have been made and the markings dried for a few minutes, the markings are heated in the hottest point of the Bunsen flame or in a blast-lamp flame until the markings, which frost at first, turn red. This heating will take about 1 minute. The intensity of heating will depend on the piece of apparatus and the kind of glass, but with more intense heating, a better etching is obtained.

On cooling, the etching is a heavy white frosting, some of which will wear off, but there will remain a good permanent white etching which will not be removed by daily washing in acid, alkali, or soap. The heavy frosting appears to become still more permanent if allowed to stand a few days before being washed.

Marking of Flint Glass or Cheap Glass Bottles

Cheap glass bottles cannot be heated as described above without considerable breakage. If the cheaper glass bottles are heated to about 55° C. (by placing on a steam radiator or in a 55° C. oven), or a temperature that can be just comfortably held in the hand, the markings can then be burned in quite satisfactorily without breakage. Of course one cannot heat as hot as with Pyrex apparatus.

If a light etching is satisfactory, the burning need be only sufficient to cause the sodium silicate marking to frost solidly. In this case, the frosting will easily wash off but will leave a distinct but fainter etching than where more heat is applied.

[1] Received April 8, 1931. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Analysis of Fatty Modifications Obtained by Action of Sulfuric Acid[1]

Melvin DeGroote, Bernhard Keiser, Arthur F. Wirtel, and Louis T. Monson

Tretolite Company, St. Louis, Mo.

The industrial modification of unsaturated vegetable and animal oils, fats, and fatty acids by means of sulfuric acid is important in the production of various commercial products. In addition, the so-called sulfonation of oleic acid bodies has been practiced in the past in arts in which its use has become obsolete.

This paper summarizes and evaluates information scattered throughout the literature. It also shows that certain conventional methods of analysis are not suitable for the examination of all fatty modifications produced by the so-called sulfonation process, and that the use of such methods causes misleading assumptions as to the fundamental composition of the various products.

New facts and methods are presented which, while they do not solve the problem of composition, it is believed will be found accurate, novel, and helpful to those engaged in the manufacture or analysis of such products.

It is shown that, although an ultimate determination of the composition of a fatty modification is not always possible, and although the identification of the parent oil is often difficult, modification can always be recognized.

The industrial modification of unsaturated vegetable and animal oils, fats, and fatty acids by means of sulfuric acid is important in the production of various commercial products, including textile oils such as Turkey-red oil, leather oils, cutting oils, plant sprays, sheep dips, emulsifying and deëmulsifying agents, and furniture polishes. In addition, the so-called sulfonation of oleic acid bodies has been practiced in the past in arts in which its use has become obsolete. For example, for years attempts were made to prepare a suitable solid candle material from oleic acid by sulfuric acid modification (*26*). Then, too, while Twitchell's original patent on fat-splitters (*42*) was for a "sulfoleic acid" (which differs from the presently known sulfoleic acid), this has been entirely superseded by more effective reagents.

Purpose of Paper and Use of Terms

The purpose of this paper is threefold—namely, to show that certain conventional methods of analysis, suitable for some textile oils, are not suitable for the examination of all fatty modifications produced by the sulfonation process; to explain that such methods may give results which cause misleading assumptions as to the fundamental composition of the various products; and finally, where methods heretofore employed have proved unsatisfactory, to submit new methods which are valuable, not only in giving more accurate analytical data, but also in indicating more clearly the probable composition of the modified fatty materials.

The term "modification" as used in this paper refers to a change in the fatty residue or fatty chain, and includes all the substitution and addition products obtained by the action of sulfuric acid on unsaturated oils, fats, and fatty acids. These modifications are characterized by the fact that they retain the fundamental chemical properties of the parent material, as indicated by the conventional constants, such as the acetyl number, saponification number, acid number, iodine number, etc., although these constants may be altered in numerical value. The modifications also retain many physical properties of the parent material, such as odor, greasiness, and viscosity. Such modifications, including, for example, hydroxystearic acid, sulfoleic acid, sulforicinoleic acid, and polyricinoleic acids, bear a simple genetic relationship to the material from which they were derived. "Modification" does not include reactions involving solely the hydrogen of the carboxyl group or its equivalent, such as soap-making or fat-splitting.

In most cases, sulfonation of an unsaturated oil, fat, or fatty acid is carried out at low temperatures, usually below 35° C. The procedure is, in short, to introduce concentrated sulfuric acid or oleum into the fatty body, with cooling if necessary, and in the presence of various catalytic or solvent materials if desired. Stirring is essential to prevent local concentrations of acid and subsequent heating, which produce "over-sulfonation." When the mass has been so treated it may be washed at once or after considerable standing, in order to remove the excess of sulfuric acid, by employing either water or a solution of sodium sulfate. Occasionally other wash solutions are used, but the usual procedure is to wash once with water and, if a second wash is used, to employ sodium sulfate. The product so obtained is neutralized wholly or in part by means of caustic soda, potash, or ammonia.

Strictly speaking, the reaction is not a "sulfonation"—i. e., it does not produce sulfonic acids, except when it is conducted at or near the boiling point of water. It does produce "sulfated" oils, however, and ought to be called a "sulfation" process, which is the nomenclature sometimes followed (*9, 16, 36*). Although the terms "sulfoleic acid" and "stearic acid hydrogen sulfate" are applied to the fatty acid sulfate derived from oleic acid, it would be better to refer to the material as "hydrogen sulfate stearic acid," or "oleic acid hydrogen-hydrogen sulfate." Likewise, the sulfated product derived from castor oil, and commonly called "sulforicinoleic acid" or "hydroxystearic acid hydrogen sulfate," should more properly be termed "hydrogen sulfate hydroxy-stearic acid," or "hydrogen sulfate oleic acid," depending on whether the sulfuric acid reacts at the double bond or at the alcoholic hydroxyl. But the term "sulforicinoleic acid" is of value in designating the fatty acid sulfates derived from castor oil without indicating the particular point of combination. The expression "sulfo acid" is employed in this article to indicate a sulfur-containing fatty acid. Use of the terms "sulfoleate" and "sulforicinoleate" in this paper is restricted to the compounds neutralized only to methyl orange. In them, the carboxyl hydrogen is still present.

[1] Received January 27, 1930. Resubmitted April 29, 1931. Practically all the data submitted in the various tables, such as constants of purified materials, analytical data on organic sulfur, iodine numbers, etc., are taken from the notebooks of Bernhard Keiser and Arthur F. Wirtel, and represent only a fraction of the work which they performed in the course of various research investigations they conducted in this laboratory. The remainder of the data are taken from the notebook of Louis T. Monson. All these investigators have employed these methods in a large number of analyses. The general discussion of fatty modification and its commercial aspects has been presented by Melvin DeGroote.

Summary and Evaluation of Previous Information

There is no suitable method for examining the unwashed reaction mixture so as to determine whether or not commercial sulfation has completely converted all fatty materials into acid sulfates. This is not so important industrially, however, because sulfation must be followed by washing, a process that is decidedly hydrolytic in character. The percentage of fatty acid sulfate in the washed fatty material is more important. The non-sulfur-containing fatty material consists of liberated or non-sulfated unsaturated fatty material, hydroxylated fatty bodies derived from acid sulfates, and derivatives of hydroxylated material, such as stearolactone, anhydrides, and poly-acids.

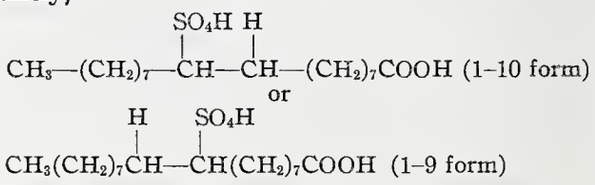
The washed fatty material, freed from excess sulfuric acid, will generally contain up to 30 per cent of fatty acid sulfate. Such material can usually be neutralized with a suitable base without further extensive hydrolysis. The water solution of the salt, properly neutralized to methyl orange, can be extracted with ethyl ether so as to free it from extraneous fatty material, and the aqueous solution of the salt can then be concentrated without decomposition.

Sulfation of a glyceride, and particularly a tri-glyceride such as castor oil, becomes complicated because of possible partial hydrolysis of the glyceride. This fact suggests a possibility of free glycerol or a glyceryl radical being present to make analytical calculations more complicated. In all cases, analysis may be made more difficult by the presence of water, mineral acid, hydrocarbons, and inorganic salts. Equally difficult is an attempt to differentiate the non-sulfur-containing materials and, more especially, the various dehydration bodies. This latter class includes stearolactone, poly-acids, anhydrides, etc.

Fortunately, many of the valuable properties possessed by fatty modifications are due to the fatty acid sulfates present; likewise, the hydroxy bodies are resultant from the acid sulfates; and the dehydration bodies are derived from the hydroxylated materials. For this reason, the investigation of fatty modification is concerned most intimately with the composition of the fatty acid sulfates, and more particularly with the residual sulfur-containing material which remains after the washing process, even though it represents only a fraction of the total washed fatty matter.

Constitution of the Sulfo-Acids

When sulfuric acid of sufficient concentration acts upon oleic acid in the cold, there is produced, by the addition of sulfuric acid at the double bond, sulfoleic acid or hydrogen sulfate stearic acid. Two isomeric forms may result—namely,



While a portion of the sulfoleic acid may consist of the latter form, investigators in this laboratory have reached the conclusion that the greater proportion of the water-extractable sulfoleic acid is the 1–10 form. This conclusion is based on the following facts.

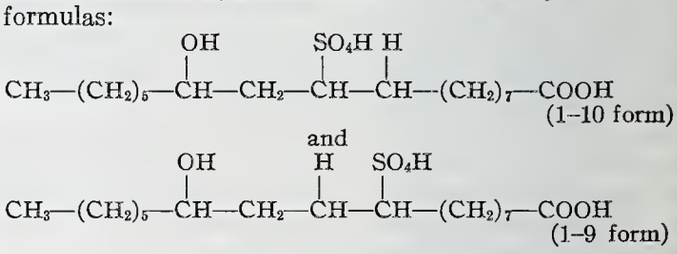
The reaction mixture of oleic and sulfuric acids was washed with water so as to remove excess sulfuric acid, and neutralized with caustic soda (to methyl orange). It was then dissolved in water, and extracted repeatedly with ethyl ether so as to yield an aqueous solution of sodium sulfoleate. This sodium salt was isolated by evaporation of the water at a maximum temperature of 50° C., and was found to contain 1.2 per cent sodium sulfate and 3 per cent water. A sample was then hydrolyzed by means of mineral acid to produce hydroxystearic acids, which were subsequently purified by four crystallizations from a mixture of 20 per cent acetone and 80 per cent petroleum ether. The constants, expressed in Table I, are indicative of 1–10 hydroxystearic acid; hence, most of the water-soluble material must have been the 1–10 sulfoleic acid.

Table I—Constants of Product Obtained from Sodium Sulfoleate

	Found	Theoretical
Acid number	187.5	187.0
Saponification number	188.1	187.0
Iodine number	2.0	0.0
Acetyl number	163.8	164.0
Melting point[a]	81.5° C.	81–82° C.

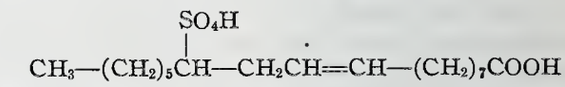
[a] The "theoretical" melting point given is that found by Tomecko and Adams (*40*), who showed that the melting point of 1–9 hydroxystearic acid is considerably lower (74–75° C.), and that a mixture of 70 per cent 1–10 hydroxystearic acid and 30 per cent 1–9 hydroxystearic acid melted at 74–76° C.

Castor oil is a hydroxylated unsaturated fatty body. One would expect it to form sulfo acids which correspond to the two sulfoleic acids, and which are indicated by the following formulas:



Since the glyceryl radical is not always entirely removed as glycerol, the acids represented by the above formulas may be present in various combinations with this radical. These are disregarded for simplicity and because glycerides were not found to be present in the samples investigated.

Benedikt (*3*), however, originally pointed out that preferential sulfonation appears to take place at the alcoholic hydroxyl rather than at the double bond. Although Juillard (*17*) has shown that sulfonation can also occur at the double bond, most later investigators have accepted Benedikt's conclusion and have assumed that sulfation takes place at the hydroxyl group only. Thus it is quite customary in the literature to consider the sulfo acid from castor oil as being an unsaturated acid of the following formula:



Data accumulated in this laboratory indicate that sulfation also takes place in part at the double bond, thus confirming Juillard's early conclusions. Sulfo acids obtained from the action of 43 per cent by weight of 66° Bé. sulfuric acid on castor oil at 35° C. were converted into the sodium salts by means of caustic soda, neutralizing only the strong acid hydrogen by using methyl orange as indicator. They were then purified by extracting the impurities from a water solution with ethyl ether, and analyzed after dehydration. The results are shown in Table II.

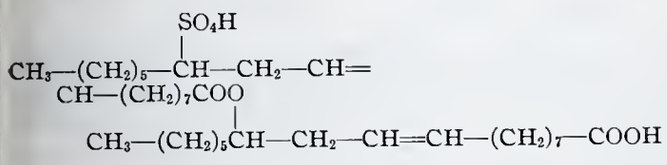
Table II—Constants of Sodium Sulforicinoleate

Glycerides	None
Water solubility, calcium salt	None
Acid number	95.1
Saponification number	138.8
Ester number by difference	43.7
Iodine number	43.0
	%
Total SO_3 by HCl-boiling	16.04
Free sulfate as SO_3	1.20
Organically combined SO_3 by difference	14.84
Organically combined SO_3 calcd. to unsaturated sodium sulforicinoleate (mol. wt. 400)	74.2
Same calculated as saturated salt (mol. wt. 418)	77.5
Ester number calcd. to ricinoleic acid	23.1

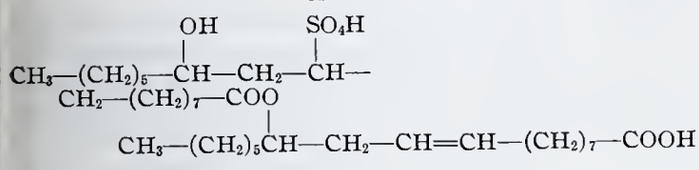
This purified acid sodium salt, when saponified and reacidified, produced an ether extract equivalent to 21.3 per

cent of the original, having an iodine number of 80.0 and an acid number of 189.5. This was evidently ricinoleic acid; and the amount compares favorably with that calculated from the ester number.

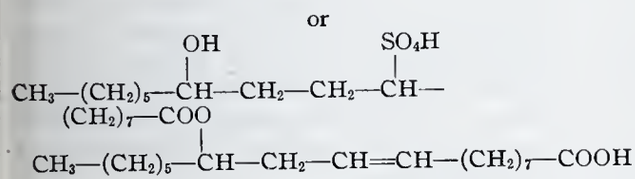
Since the presence of a body that produces ricinoleic acid by saponification and subsequent acidification can be explained by the existence, for example, of one of the following three compounds, no percentage composition is attempted.



or



or



The ricinoleic acid residue of such compounds will account for only approximately 20 units of the iodine number. The balance of this value must be explained by the presence of an unsaturated sulfo acid. The fact that this remainder (approximately 23) was far below 63.5, the theoretical value for the sodium salt of the unsaturated sulforicinoleic acid, shows that some of the sulfuric acid has been added at the double bond. The prior experiment was repeated in duplicate, and confirmation of the results was obtained.

Investigation in this laboratory has failed to reveal a disulforicinoleic acid, in which sulfuric acid residues are present at both the double bond and the alcoholic hydroxyl of one molecule.

Sulfoleic acid and sulforicinoleic acid are both acid sulfates, as stated before. Unlike the true sulfonic acids, they are unstable and are decomposed on boiling with water or in the presence of mineral acids, with the production of sulfuric acid. Both have titration curves showing two breaks: one for a strong hydrogen ion, titratable to methyl orange; and one for a weak hydrogen ion, titratable to phenolphthalein. When the sulfo acids are shaken with neutral saturated salt solution, they are gradually neutralized and salted out with the production of hydrochloric acid and the respective sodium salts (*18*, *37*, *41*). The carboxylic hydrogen is never neutralized in such decomposition reactions. The sulfo acids are not truly soluble, but are colloidally dispersible in water, and are salted out by the addition of mineral acids or salts. Their alkali salts show the same property. The acids and their alkali salts form precipitates with soluble calcium salts, although these phenomena are frequently obscured by the action of an excess of the protective colloid (*33*). Incidentally, the molecular weight of sulfoleic acid is 380, while the unsaturated and saturated forms of sulforicinoleic acid have molecular weights of 378 and 396, respectively.

If, as is generally believed, all of the organically combined sulfur were present in such forms as given above, the matter of composition and analysis of sulfated oils would be greatly simplified. The methods widely accepted for the determination of total sulfur depend upon the decomposition of the sulfo acids by means of mineral acids. It has been found in this laboratory, however, that by using the sodium peroxide bomb of Parr on sulfated oils, values can be obtained that are as much as 50 per cent greater than results obtained by any of the methods depending on decomposition by boiling, even for excessive periods, with mineral acid, such as concentrated hydrochloric acid. Both methods are suitable for fatty acid hydrogen sulfates or their salts, as indicated by results obtained on the purified salts, and also on the salts in presence of added fatty bodies.

Table III—Comparison of Methods for Determining Total Sulfur
(Values given as per cent SO_3)

Sample number	1	2	3	4	5	6	7	8	9	10
HCl-boiling	1.93	5.16	2.18	8.45	1.01	2.18	1.16	1.17	18.46	16.04
Parr bomb[a]	3.34	5.52	3.50	9.06	2.16	2.85	1.92	2.41	18.49	16.16
Parr bomb on HCl - boiled sample	1.30									
Saponified sample boiled with HCl		5.29								
HCl-boiled sample saponified, reboiled, HCl	0.21									
Same procedure repeated	0.00									
Parr bomb on sample saponified after HCl-boiling			0.89							

[a] Sample of unmodified castor oil showed no sulfur by this method.

Samples 1, 4, 6, 7, and 8 were castor oil products.
Sample 2 was an oleic acid product.
Samples 3 and 5 were of unknown origin, probably castor oil.
Sample 9 was purified potassium sulfoleate.
Sample 10 was purified sodium sulforicinoleate.
Addition of castor oil or oleic acid to samples 9 and 10 did not prevent complete liberation of sulfuric acid by the boiling method.
Results on samples 9 and 10 are below theoretical because these samples contained small amounts of water.

These observations clearly indicate the presence of organic sulfur in some sulfated oils in some form that is not decomposable by boiling in the presence of mineral acid. The complications arising from attempting to calculate the composition of sulfur-containing constituents on the basis of those components previously assumed to be present are obvious enough, and become more involved by attempting to compensate for this newly discovered form of non-decomposable organic sulfur.

Similar complications arising in attempting to interpret other determinations on non-sulfur-containing materials make an ultimate analysis practically impossible. Frequently the parent oil cannot be determined with accuracy (*7*), as seen by the values in Table IV, obtained from the sulfation of a single oil, castor oil, under varying conditions of manufacture.

Table IV—Constants of Oil Obtained by Boiling Sulfated Castor Oil with Hydrochloric Acid

Sample number	1	2	3	4
Acid number	95.6	141.5	117.5	101.2
Saponification number	192.9	201.2	192.0	186.5
Ester number	97.3	59.7	75.5	85.3
Iodine number	42.0	74.0	67.1	38.0
Acetyl number	74.2	106.8	63.4	50.0

One statement can be made. The presence of organically combined sulfur is almost certain proof that the material has been modified. Even in the absence of combined sulfur, the products obtained by modifying fatty materials show chemical and physical constants that do not coincide exactly with those exhibited by any known naturally occurring oil or fat, or mixtures thereof.

Discussion of Improved Analytical Procedure

The preceding discussion is believed to summarize information distributed throughout the literature and to evaluate it. In addition, new facts and methods that have never been published before have been presented. In the succeeding sections, improved analytical procedures are discussed. While these do not solve the problem of the composition of sulfated oils, they are presented with the conviction that they will prove distinctly helpful to those engaged in the manufacture or analysis of such products.

Estimation of Combined Sulfur

As mentioned previously, the estimation of combined sulfur is probably the most important determination to be made on sulfated oils as well as on the washed unneutralized reaction mass during process of manufacture. Reference is had, of course, to organically combined or organically bound sulfur, which, while it is almost always present, may be entirely absent after the reaction product has been washed with water.

The earliest method of estimating the amount of sulfo acid present was to dissolve a sample of the reaction mass in water. If the solution (dispersion) produced was entirely clear, it was presumed that the fatty material had been completely sulfonated. This is not necessarily true, because as little as 20 per cent of sulforicinoleic acid will produce an oil that gives a clear water dispersion. If the sample has been neutralized, even in part, the salts then present promote the water dispersibility, so that even less sulfo acid is required to produce a clear dispersion.

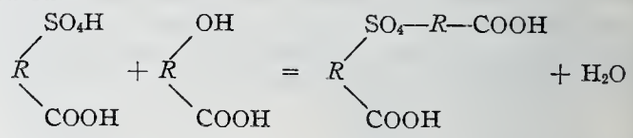
The usual method is to determine combined sulfur by difference, by first determining total sulfur, and then subtracting the "free" sulfur—i. e., the sulfur present as sulfuric acid, or in the case of neutralized oils, as sulfates. Sulfur in this latter form can be determined easily and accurately. Total sulfur has been determined in this laboratory by various methods; for example, by the use of the sodium peroxide bomb of Parr, the oxygen bomb, the Eschka method, the lamp method, the hydrochloric acid–boiling method, and the double titration method, the results of which are subsequently detailed. The double titration method, when used on neutralized or partially neutralized material, is also known as the "American method."

Parr Bomb Method—Of all these methods, the one that gives the highest results for total sulfur in both oleic acid and castor oil products is the Parr bomb method. The procedure for this determination is the conventional one used in the examination of petroleum oils, although the use of the peroxide bomb in the analysis of fatty modifications has apparently not heretofore been recorded in the literature.

Hydrochloric Acid–Boiling Method—The most widely accepted method for determining total sulfur is to boil the sample with hydrochloric acid until all the sulfur-containing compounds that are susceptible to decomposition with mineral acids have been decomposed with the formation of sulfuric acid. The aqueous layer is separated from the fatty matter, and the sulfuric acid is precipitated as barium sulfate, according to the conventional method (*21*). Any emulsion formed may be decomposed by the use of a 10 per cent salt solution.

This method gives concordant results if the boiling is vigorous and is continued sufficiently long to decompose all the unstable sulfur compounds. To prevent loss of sample by bumping, porous plate cannot be used, as it absorbs considerable acid. Continuous shaking by hand or by means of a gentle stream of air is recommended. The hydrochloric acid lost by evaporation should be replaced to prevent charring or any sulfonation due to the increasing concentration of the free sulfuric acid.

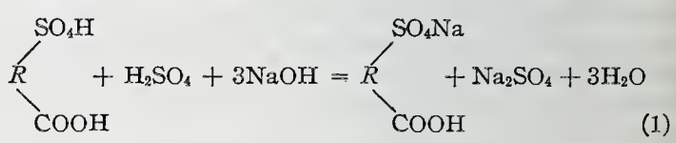
Results on certain classes of sulfated oils are uniformly lower than those obtained by the peroxide bomb method. The only explanation of this fact is that all the sulfur in organic combination in such oils is not split off during the boiling process, regardless of how long this is continued. Treatment of the fatty material, separated by the boiling process, with alcoholic potash in a saponification procedure, followed by a second hydrochloric acid boiling, will produce a small additional amount of sulfuric acid. Repetition of this procedure does not recover any additional sulfur, as is shown in Table III. Whether this increment represents sulfur that was originally present in a compound produced by the condensation of sulfoleic or sulforicinoleic acid and a hydroxy acid in the following manner can only be conjectured:



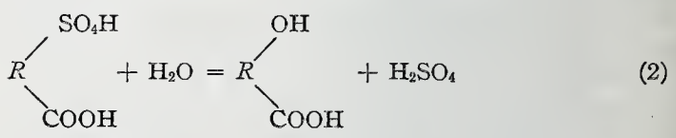
Since the oily layer recovered from the first hydrochloric acid boiling is not acid to methyl orange, it is certain that the additional sulfur obtained was not present in the oil as either free sulfuric acid or as a sulfonic acid not susceptible to decomposition with mineral acid.

The disagreement of results is noticeable in both oleic acid and castor oil sulfations, but is much more pronounced in the latter. The hydrochloric acid–boiling method gave results that were only 60 per cent of those obtained by the bomb method, when the two were compared on several castor oil products. On oleic acid products, the difference was not so marked, but was appreciable. It should be pointed out that on samples of carefully purified potassium sulfoleate and sodium sulforicinoleate the two methods gave identical results, even in the presence of added fatty material, showing that they are both valid where only this type of sulfur-containing compound is to be dealt with.

Double Titration Method—If, in the analysis of an unneutralized washed reaction mass, a standard solution of sulfuric acid is used instead of hydrochloric acid in the boiling process, the precipitation of barium sulfate may be replaced by the titration of the liberated acid to methyl orange, making proper deduction for the amount of standard acid added to promote the decomposition. This method depends on the following reactions:



(1)



(2)

Titration of a sample of the washed reaction mass in the cold, using methyl orange as indicator, will give the amount of standard alkali required for the sulfo acid and the free sulfuric acid present, according to Equation 1. Boiling with standard acid will convert the sulfo acid into free sulfuric acid and a fatty acid or fatty body free from sulfur. This is a hydrolytic action, and is shown by Equation 2. The standard acid added is not shown in this equation, since all that is added is subsequently accounted for, in calculating the amount of sulfur present in the form of decomposable organic bodies.

The boiling process results in an increase of one equivalent of methyl orange acidity for every molecule of sulfo fatty acid present as can be seen from Equation 2, since one molecule of monobasic (to methyl orange) sulfo acid decomposes into one molecule of dibasic sulfuric acid. The difference between the two titrations represents the alkali required for the sulfo acid.

The same method can be applied to the analysis of neutralized or partially neutralized samples, in which form it is known as the "Hart method (*10*)" or the "American method (*12*)." The only difference involved in using it in the analysis of neutralized products is that the alkali present must be taken into account. If sufficient alkali has been used to neutralize

some of the carboxylic hydrogen in addition to all of the strong acid hydrogen, then the amount of acid present after boiling is equal to the total amount of acid less the amount of acid necessary to neutralize the alkali formerly combined with the carboxyl.

The procedure is as follows:

Shake an ethyl ether solution of the oil, known to be partially or wholly neutralized, with standard sulfuric acid, draw off the acid layer, and wash the ether solution free from acid with neutral salt solution. Titrate the acid and washings to a methyl orange end point with standard caustic. Call the decrease of acidity, expressed as milligrams of KOH per gram, *A*. This represents the amount of caustic attached to the carboxyl group. (This procedure is a modified one developed in this laboratory, for the reason that the titration method recommended originally is tedious.) A second sample of the oil is boiled for 40 minutes with a known excess of standard sulfuric acid. If ammonia is present, the mixture of an ethereal solution of the sample and the added acid must be thoroughly shaken in the cold. The ether is then removed before boiling. If this precaution is not taken, some "carboxyl ammonia" may be lost owing to the fact that the added acid has not reacted with the ammonium salts because of incomplete mixing. On cooling, the oily layer is taken up in ether, the acid layer is withdrawn, and the ether solution is washed free from acid. (In the Hart method, the oil is not separated before titrating.) The combined extract and washings are titrated with standard caustic. The amount of caustic required for the standard acid, added before boiling, is deducted. The remainder is called *F*, and is also expressed as milligrams KOH per gram. It is obvious that this value may be either positive or negative, depending on the amount of alkali present as "carboxyl alkali." If this is less than sufficient to combine with the sulfuric acid liberated, there will be an increase in acidity of the water layer on boiling, and *F* will be positive. If there is an excess of alkali over that required to combine with all the sulfuric acid produced, there will be a diminution of acidity, and the titration will require less standard caustic for the methyl orange end point than the equivalent of the amount of standard acid added. In this case, *F* is negative. The algebraic sum of *A* and *F* represents the KOH equivalent of the sulfuric acid produced on decomposition.

There has been considerable controversy during the past three years (*1*, *2*, *13*) as to whether KOH was equivalent to SO_3, or whether 2 KOH were equivalent to SO_3. Herbig, supporting the latter view, made the error of confusing the fact that the SO_3 contained in sulfuric acid is equivalent to 2 KOH, with the fact that the sulfo acids contain the group, $—SO_4H$, having only one hydrogen ion titratable to methyl orange. The SO_3 in sulfo acids is equivalent to but one KOH.

Herbig also attacked the method on the ground that sulfuric acid does not completely decompose the sulfo acids in sulfated oils on boiling. This point has been investigated in this laboratory. Based on preliminary investigation, as shown in Table V, there is indication that boiling with sulfuric acid instead of with hydrochloric acid (by which modification the boiling process becomes the "*F* plus *A*" method) may convert a part of the fatty acid sulfate into a compound that is not decomposable on boiling; for this reason results are apt to be low.

Table V—Values for Organically Combined SO_3 in Sample of Sodium Sulforicinoleate

Peroxide Bomb	HCl-Boiling	*F* + *A* Method Using H_2SO_4	HCl-Boiling on Residual Oil	Peroxide Bomb on Residual Oil[a]	Total SO_3 Columns 3, 4, 5
15.0	15.0	14.53	0.00	0.44	14.99
		13.93	0.00	1.03	14.96
		13.16	0.00	1.59	14.75

[a] Corrected to original sample.

It was found that in some other instances the results obtained were in fairly good agreement with those obtained gravimetrically using the hydrochloric acid–boiling method. In others, it was slightly lower. In general, it agrees fairly well, but since the results are inclined to be slightly low, they must be accepted with caution, even when the concentration of standard sulfuric acid employed is increased from 0.5 *N* to 1.0 *N*. It is, of course, more rapid than the gravimetric method, and where speed is preferred over great accuracy (*35*), it should be adopted.

Other Methods—The lamp method (*14*), burning an alcoholic solution of the oil in a lamp, collecting the products of combustion in standard caustic, and titrating the remaining caustic to methyl orange, gave erratic and non-reproducible results. It is considered unworthy of further experimentation in attempting to use it in the analysis of sulfated oils in general.

The oxygen bomb method, recently recommended in modified form for petroleum products (*8*), was used on one sample consisting primarily of a sulfated vegetable oil. As the pressure on the bomb was increased, the values rose. In all cases they were very much lower than those obtained by the peroxide bomb method; and in some cases results were not confirmable, even at the same oxygen pressure.

The Eschka method, which requires very careful manipulation wherever it is used, was found to give low results on several samples. It was not investigated further, as there were other methods that gave greater promise.

Comparison of Methods—Of the methods that give reproducible results, the Parr bomb is believed to give the most dependable results, approximating most closely the total sulfur present. This finding does not mean, however, that the hydrochloric acid–boiling method or all of its modifications should be discarded. The hydrochloric acid–boiling method has been shown to give accurate results on pure sodium sulfoleate. From this observation, it seems fair to conclude that the difference between the values obtained by the Parr bomb and the hydrochloric acid–boiling method will indicate the amount of organically combined sulfur present in a form other than acid sulfate. In general, the adoption of any method and the acceptance of the results obtained by its use, together with the rejection of all other methods, is fraught with risk. It is recommended that both the hydrochloric acid–boiling method and the Parr peroxide bomb method be used, so that organically combined sulfur may be divided into two parts, decomposable and non-decomposable. If the investigator intends to make only one sulfur determination, he must decide which value is of greater importance, decomposable combined sulfur or total combined sulfur.

Action of Sulfuric Acid on Unsaturated Fatty Materials at Higher Temperatures

The action of sulfuric acid on unsaturated fatty materials at higher temperatures has been little studied in the past, and hence there is a paucity of information regarding it in the literature. Some of the statements that seem to refer to sulfonations at or near the boiling point of water (*22*) in reality refer to the distillation of the washed products of a reaction conducted at ordinary temperatures (*39*).

At temperatures near that of boiling water, oleic acid produces a sulfonation product quite different from the product obtained at ordinary temperatures. Instead of being an acid sulfate and unstable, it is a true sulfonic acid, and is stable to boiling with dilute acids. It is only colloidally soluble in water, as are its alkali salts. It forms the sodium salt by double decomposition on being shaken with neutral saturated salt solution. This property has been employed in this laboratory for the determination of combined sulfur in the sulfonated mass, which is so dark-colored as to preclude direct titration. Its molecular weight is assumed to be 380, and its structure is probably similar to that of sulfoleic acid except that the groups $—SO_3H$ and —OH replace the groups $—SO_4H$ and —H, respectively, although Twitchell has suggested an ester acid formula for the body (*43*).

In the analysis of an unneutralized sample of oil sulfonated at or near the boiling point of water, five determinations are made. Sulfur dioxide is distilled into standard caustic and estimated. An ether solution of a second sample is washed with saturated salt solution until neutral to methyl orange and the free sulfuric acid is precipitated as barium sulfate. Since direct titration of the very dark-colored solution for total acidity is almost impossible, the same procedure is adopted on a third sample. This is washed with neutral saturated salt solution until the washings become neutral to methyl orange, whereupon they are titrated with standard caustic. The value obtained represents sulfur dioxide, free sulfuric acid, acid sulfate, and true sulfonic acid. By precipitating the sulfur present in the washings after titration, the use of a separate sample for the determination of the free sulfuric acid can be obviated. A fourth sample is boiled with a known amount of standard sulfuric acid until all the decomposable acids are hydrolyzed. The mixture is shaken with ether and the aqueous layer withdrawn. The ether layer is washed with saturated salt solution until free from mineral acid and the combined aqueous extracts are titrated. The amount of standard caustic consumed (corrected for the amount of standard acid added) will be larger than that obtained in titrating the preceding sample, by the amount of acid produced by the decomposition of the sulfoleic acid, but will be smaller by the amount of sulfur dioxide evolved during boiling. From these determinations the decomposable sulfo acid can be estimated. The true sulfonic acid is obtained by difference. Actually, in products produced at this temperature, no acid sulfate was detected by the above method. When the sum of the values for sulfur in these four forms, as properly calculated, is subtracted from the total sulfur as determined by the Parr peroxide bomb, there is obtained a fifth value—namely, non-decomposable non-acidic organically combined sulfur.

The same procedure may be adapted to the analysis of sulfated oils in mixture with such fatty sulfonic acids. As has been pointed out, however, there are indications of the existence of sulfur in some neutral form, in addition to that which is present as sulfoleic or sulforicinoleic acid or other acid sulfate and sulfuric acid, in the products produced at ordinary temperatures.

Briefly, then, the conventional methods heretofore employed are incorrect in many instances where commercial products are being examined. The older mineral acid–boiling methods do not always give true total sulfur. Such methods give free sulfur plus organically bound decomposable sulfur. Investigation has revealed that the only suitable method for true total sulfur is the peroxide bomb method. Furthermore, deducting the sum of free sulfur and decomposable sulfur (formerly called "total sulfur") from the true total sulfur obtained by the peroxide bomb method gives a new index of comparison, the non-decomposable organically bound sulfur.

In all cases, in the very exact determination of sulfur in the washed unneutralized reaction mass, one must recognize the presence of a very small amount of sulfur in the form of sulfur dioxide. In the ordinary sulfation process, this quantity is negligible, since the temperature is held at such a level as to prevent the formation and the evolution of the gas. In "over-sulfonating"—i. e., in using a large excess of sulfuric acid, or at higher temperatures, the amount of sulfur dioxide produced becomes appreciable. It may be determined by distilling a water solution of a weighed sample into standard caustic and titrating to methyl orange.

Methods for Other Determinations

Ammonia—The usual method for ammonia in soap, shaking with dilute acid and distilling the extract into standard acid after liberating the ammonia with caustic (*19*), is accurate and applicable to the determination of ammonia in sulfated oils, but it consumes more time than a second method suggested first by Welwart (*45*) and more recently by Lang (*20*), as a result of his work in this laboratory. The method is to add an excess of caustic soda solution and a solution of calcium chloride to the sample in a Kjeldahl flask and to distil the ammonia liberated thereby into standard acid. The calcium chloride effectively prevents frothing during distillation by forming lime salts.

These determinations give values for total ammonia, including that present as ammonium sulfate and the ammonium salt of the sulfo acid, in addition to that combined with the carboxyl group. The ammonia combined in this last form is frequently more important than the total ammonia.

This "carboxyl ammonia" may be determined, as in the Hart method for combined sulfur, by titrating a sample with acid in the presence of salt solution and ether, but this method is not so rapid nor accurate as a modified procedure developed in this laboratory. Instead of titrating the sample with acid, it is better to shake its ether solution with standard acid, then wash with salt solution, and subsequently determine the amount of standard acid consumed, by titrating the aqueous layer and the washings from the ether layer with caustic. The decomposition phenomenon previously observed enters into this method only in an indirect fashion. When the standard acid is added to the sample, some of the ammonia in combination with the strong hydrogen of the sulfo acid combines with the sulfuric acid added, and only on repeated washing with salt solution is it possible to obtain a neutral product. The effect of this action need not be accounted for in the calculation, inasmuch as the sulfuric acid consumed in combining with the ammonia formerly attached to the sulfo acid is replaced, on washing, by an equivalent amount of hydrochloric acid.

The method is applicable, also, to the determination of sodium and potassium combined with the carboxyl group. An ash determination will give the total amount of alkali, part of which will be found in the ash in the form of sulfate, and part as carbonate.

Iodine Number—One of the first determinations used in the analysis of sulfated oils was the iodine number. Theoretically, the more oleic acid is modified, the smaller the iodine number becomes, as can be seen from the preceding discussion. It has been shown that castor oil yields saturated as well as unsaturated sulfur-containing bodies, for which reason the iodine number of the sulfated mass will be found considerably lower than that of castor oil. Some samples of sulfated castor oil have been found in this laboratory to have iodine numbers as low as those of products obtained by the sulfation of oleic acid, which indicates the difficulty encountered in attempting to use this constant in fixing the origin of any particular sample of sulfated material.

There are a number of methods for determining the iodine numbers of unmodified fatty materials. These methods include those of Hübl, Hübl-Waller, Wijs, and Hanus. Broadly speaking, these methods are acceptable for the majority of unmodified fatty materials, such as red oil and olive oil. It is peculiar that when certain of these standard methods are applied to fatty modifications, the iodine numbers obtained vary with the size of sample employed in the determination itself. This lack of constancy precludes the acceptance of such methods. The investigators in this laboratory have studied a number of other methods, such as the Margosches method (*31*), the pyridine sulfate dibromide method of Rosenmund (*38*), and certain recorded variations of the Wijs method, such as the Wijs solution with excess of iodine and the Meigen and Winogradoff modification (*32*). Likewise, such variations of standard methods which included

variation in time of reaction, solvent employed, etc., were studied.

Table VI—Iodine Number of Sulfated Castor Oil Washed So As to Hydrolyze Completely All Fatty Acid Sulfate
(Solvent used, CCl_4, except as noted)

Method	Time	Sample	Iodine Number	Corrected Iodine Number[a]
	Minutes	*Gram*		
Hanus	30	0.192	67.3	
		0.294	57.0	
		0.430	48.4	
Hanus[b]	30	0.100	84.2	
		0.318	70.1	
		0.315	63.4	
Wijs (normal)	30	0.250	64.3	
		0.409	57.7	
		0.441	56.4	
Wijs (normal)	30	0.203	60.2	
		0.291	56.3	
		0.407	51.3	
Wijs (normal)	60	0.208	68.0	
		0.302	63.7	
		0.436	56.7	
Wijs (2% iodine excess)	30	0.094	62.4	
		0.245	59.2	
		0.488	47.5	
Wijs (2% iodine excess)	15	0.127	58.0	
		0.267	54.2	
		0.329	53.0	
Rosenmund	3	0.142	58.0	
		0.275	54.2	
Rosenmund	3	0.120	59.2	
		0.244	56.2	
		0.357	54.0	
Rosenmund	10	0.161	79.5	
		0.270	59.6	
		0.370	57.5	
Meigen-Winogradoff	30	0.171	140.0	−33.0
		0.300	88.0	−10.0
		0.613	48.6	− 0.5
Meigen-Winogradoff	30	0.058	198.0	−14.0
		0.200	113.0	−48.0
		0.326	74.5	− 6.5
Meigen-Winogradoff	30	0.144	161.0	−26.0
		0.182	145.0	−23.0
		0.473	63.0	− 1.0
Meigen-Winogradoff	30	0.083	186.0	−59.0
		0.168	135.2	−31.0
		0.281	86.5	−10.0
	Hours			
Hübl	4	0.139	28.2	
		0.223	28.3	
		0.361	29.3	
Hübl	24	0.136	32.6	
		0.252	34.2	
		0.328	33.7	
Hübl-Waller	2	0.110	27.6	
		0.179	27.6	
		0.272	28.1	
Hübl-Waller	24	0.165	37.0	
		0.342	37.3	
		0.584	35.4	
	Minutes			
Margosches[c]	5	0.074	38.0	
		0.179	38.4	
		0.325	37.0	

[a] The Meigen-Winogradoff modification of the Wijs iodine-number method involves a correction which gives negative values on certain castor oil modifications.
[b] Solvent used, chloroform.
[c] Solvent used, alcohol.

In order to eliminate the possible effects of the presence of fatty acid sulfates, water, and dilute sulfuric acid, a series of tests was conducted on a modification derived by the action of sulfuric acid on castor oil, with subsequent hydrolysis so as to decompose all the acid sulfate and also to eliminate the presence of water and sulfuric acid. In the manufacture of fatty modifications, the analyst is often concerned with the composition of the unneutralized washed fatty material which usually contains some fatty acid sulfate, and generally some acidulated wash water which has not completely separated on standing. It was expected that the results on this hydrolyzed and almost water-free sample would show closer agreement than if a washed unneutralized sample of the reaction mass had been selected, owing to the elimination of the indicated factors which might affect results. The results are shown in Table VI. The same results were obtained on samples of other modifications, but are not shown for the sake of brevity.

Table VI shows that the various methods, such as the Hanus, Wijs, modified Wijs, Rosenmund, Hübl, and the Meigen and Winogradoff variation of Wijs method, are not acceptable for determining the iodine numbers of fatty modifications derived from castor oil. The table also shows that the Hübl-Waller solution, when used, should be allowed to stand 24 hours in contact with the unsaturated oil. Further experimentation, not included in the table, indicated that the Margosches solution should be allowed to react at least 3 minutes and not more than 5 minutes with the unsaturated oil. The table indicates that the Hübl-Waller method and the Margosches method are applicable to fatty modifications derived from castor oil, provided fatty acid sulfates, sulfuric acid, and water are absent.

Table VII shows the result of tests in which the Margosches method and Hübl-Waller method were applied to a mixture of 90 per cent castor oil and 10 per cent dilute sulfuric acid, so as to determine the influence of sulfuric acid and water on the results obtained.

Table VII—Iodine Number of Castor Oil-Dilute Sulfuric Acid Mixture

Sample	Hübl-Waller	Sample	Margosches
Gram		*Gram*	
0.117	76.1	0.106	89.0
0.221	76.5	0.211	80.5
0.362	75.8	0.330	73.0

These results demonstrate that the Hübl-Waller method is acceptable, whereas the Margosches method is not acceptable. It must be noted, however, that Margosches recognized that his proposed method was not entirely suitable for castor oil alone, even in absence of water and sulfuric acid (*31*). The same results were found in this laboratory. The Margosches solution, on a sample of castor oil weighing 0.083 gram, gave an iodine number of 94, whereas, on a sample weighing 0.206 gram, it gave an iodine number of 85.

Table VIII presents the results obtained by using the Margosches method as well as the Hübl-Waller method on a sample of substantially pure sodium sulforicinoleate obtained from a sulfated castor oil. For a complete analysis of the sodium salt, see Table II.

Table VIII—Iodine Number of Sodium Sulforicinoleate

Sample	Hübl-Waller	Sample	Margosches
Gram		*Gram*	
0.114	42.6	0.146	43.5
0.354	43.0	0.207	43.5
0.558	43.0	0.498	43.1

Table IX—Comparison of Iodine Number Determined by Hübl-Waller and Margosches Methods

	Hübl-Waller Method			Margosches Method		
Sample	Time	Sample	Iodine number	Time	Sample	Iodine number
	Hours	*Gram*		*Minutes*	*Gram*	
1	24	0.165	37.0	5	0.074	38.0
		0.342	37.3		0.179	38.4
		0.584	35.4		0.325	37.0
2	24	0.149	41.7	5	0.182	45.8
		0.378	41.3		0.291	42.5
		0.477	40.3		0.395	41.2
3	24	0.202	73.6	5	0.122	75.0
		0.283	74.5		0.240	75.0
		0.394	74.4		0.313	72.0

Table VIII shows that the presence of neutralized sulfated oil does not appear to affect the value obtained by either the Margosches method or the Hübl-Waller method.

Due to the almost prohibitive length of time required to conduct the Hübl-Waller iodine-number determination, the Margosches method was compared with the Hübl-Waller method on other sulfated oils which had been treated so as to eliminate the fatty acid sulfate, but which showed a variation in iodine number from 37 to 75. These results are shown in Table IX.

Table IX reveals the rather peculiar fact that, although the Margosches method will not check the Hübl-Waller method on castor oil itself, it appears to give concordant results on many fatty modifications derived from castor oil, especially in the absence of water and sulfuric acid. In view of the findings in Table VIII, this method is not particularly affected by the presence of a neutral fatty acid sulfate. Therefore, the conclusions, based on the four tables submitted, are that the Hübl-Waller method is the only one which is acceptable for research work. But for plant control work, where the Margosches method has been checked against the Hübl-Waller method and found to give reasonably concordant results, there is no reason why it should not be employed, in view of the fact that results are obtainable within a few minutes, as compared with the 24-hour period required by the Hübl-Waller method.

Acetyl Number and Hydroxyl Number—The acetyl number, as modified by Lewkowitsch (*27*), has been a fundamental constant in the analysis of oils, fats, and waxes. Contrary to the statement of Lewkowitsch (*28*), however, it cannot be used directly to determine the percentage of a particular hydroxylated fatty body in a mixture with non-hydroxylated fatty matter. For example, if the acetyl number of a mixture of 10 per cent hydroxystearic acid and 90 per cent of matter inert in the presence of acetic anhydride were determined, it would be found to be 18.7, instead of 16.4 (as it should be, from Lewkowitsch's assumption that it would be 10 per cent of 164, the acetyl number of pure hydroxystearic acid). This is true because there has been an increase in weight on acetylation of the hydroxystearic acid, so that it now represents 11.2 per cent of the acetylated oil instead of 10 per cent. The acetylated oil, on which the acetyl number is determined, has increased to 101.4 per cent of the weight of the original oil. The hydroxystearic acid increase in weight has been allowed for in Lewkowitsch's calculation, but the sample increase in weight has not.

Table X—Relationship between Percentage of Hydroxystearic Acid and Acetyl Number

Hydroxy-stearic Acid	Non-Acetylable Materials	Acetyl Number	Error
%	%		%
0	100	0.0	0.0
10	90	18.4	12.0
20	80	36.2	10.5
30	70	53.8	9.3
40	60	70.7	7.7
50	50	87.3	6.4
60	40	103.5	5.1
70	30	119.2	3.9
80	20	134.5	2.5
90	10	149.4	1.2
100	0	164.0	0.0

Table X makes clear the relationship between the observed acetyl number and the percentage of hydroxystearic acid, together with the percentage of error introduced by calculating the latter by the method of Lewkowitsch. A curve can readily be drawn showing the percentage of hydroxystearic acid corresponding to any observed acetyl number. The same principle may be used to determine any other hydroxylated body showing an acetyl number in simple mixture with non-acetylable material.

These difficulties of calculation would be obviated if the determination were made on a sample weighed before acetylation instead of after acetylation. This is the reason for favoring the adoption of hydroxyl number over acetyl number and defining the constant as the milligrams of KOH required by the acetic acid obtained from the acetylation and subsequent saponification of a 1-gram sample of the oil or fat under examination.

A method proposed by Normann (*11*) was found unsatisfactory. Methods involving the use of ceresin (*6*) to form a solid cake with the acetylated mass were not investigated, being complicated.

The method finally developed is as follows:

A weighed sample is refluxed with acetic anhydride in the usual manner, after which water is added to the mass in the acetylation flask, and the mixture is boiled for $^1/_2$ hour to hydrolyze the excess of acetylating agent. A slow stream of carbon dioxide is used to prevent bumping. The mixture is then transferred quantitatively to a separatory funnel, using ether, and is washed until neutral to litmus. The ether is evaporated, the oil is saponified with alcoholic potash in the usual manner, and the acetic acid is liberated by means of an amount of standard acid equivalent to the potash. The acetic acid may be estimated by either of the methods given by Lewkowitsch (*27*), or the filtration method may be modified by shaking the acetic acid out of the acidified mass, in ether solution, by means of water, and titrating.

Results are expressed in milligrams of KOH required for the acetic acid liberated from 1 gram of original oil. From this, and from the hydroxyl number of any pure hydroxylated material, the percentage of the latter can be calculated. Of course, only one single hydroxylated body can be present in the mixture if the method is to be used for calculating percentage composition.

A modification of a method proposed by Verley and Bölsing (*44*) and later adapted by Peterson and West (*34*) to the determination of hydroxyl groups in materials like sugars, was investigated without success. The method contemplates effecting acetylation by means of acetic anhydride in pyridine solution and titrating the acidity produced. The directions of Peterson and West were modified to permit the determination to be made in a few hours at temperatures up to the boiling point of pyridine, instead of allowing the reaction to take place in 48 hours at ordinary temperatures, as the method directs. The original method was too slow, although it may have given satisfactory and reproducible results.

The usefulness of the acetyl or hydroxyl number in detecting the origin of fatty matter in sulfated textile oil products is recognized. But statements in the literature, to the effect that castor oil can readily be identified thereby, as, for example, the following: "An acetyl value of 125 or above will point to pure castor oil; in case other oils have been used, lower values will be obtained (*24*)," are misleading if applied indiscriminately to other sulfation products even when derived solely from castor oil. In this laboratory, castor oil products have shown acetyl numbers as low as 30.

Lactones, Anhydrides, and Poly-Acids—Lactones are commonly determined by the difference between saponification number and acid number. In the case of sulfated oils, this is not a suitable means of determining them for the reason that other bodies present will have either a saponification number and no acid number, or will have a saponification number larger than their acid number, without containing lactones. For example, there are produced, in oleic acid sulfations, materials which show considerable "ester numbers"—the ester number being saponification number minus acid number. These, on saponification and subsequent re-acidification, do not revert to acids, and the ester number of the mass is still considerable, although it may be somewhat reduced. In castor oil sulfation products, the ester number practically disappears during this treatment. Saponification and subsequent acidification of a lactone, as differen-

tiated from anhydrides and poly-acids, would be expected to reproduce the original lactone, because lactones are generally regarded as being formed spontaneously from gamma-hydroxy acids.

When hydroxylated fatty acids, especially ricinoleic acid or the hydroxylated acids produced during the sulfation of castor oil, are heated, an esterification takes place, the alcoholic hydroxyl of one molecule of hydroxy acid reacting with the carboxyl hydrogen of another. This process is stimulated by acids, espeeially hydrochloric acid, but will proceed in the absence of mineral acid, as can be shown by the fact that ricinoleic acid isolated from castor oil gradually loses its acid number on standing, while its saponification number remains constant.

On saponifying and re-acidifying, these poly-acids or ester acids are converted into hydroxy acids, but any slight heating, especially in the presence of mineral acid, will again convert them into materials which show an ester number. For example, it has been mentioned previously in this paper that the calculation of the percentages of the actual constituents of the fatty matter of a sulfated oil is practically impossible. It is now evident that the hydrochloric acid–boiled portion of the oil, usually used for analysis, cannot represent only those constituents that were originally present because of the esterifying action that has taken place in the boiling process.

Because of the larger number of possible constituents of this nature, including lactides and glycid acids, in castor oil sulfation products, it is difficult to determine the amount of lactones present, if any. Careful manipulation and observance of precautions to prevent the formation of poly-acids will permit the analyst to obtain a value that represents only lactones and does not include poly-acids and anhydrides. This method is as follows:

The sample is saponified and the resultant salts are split with mineral acid. The liberated fatty matter is dissolved in ether and washed free of mineral acid, after which the ether is allowed to evaporate at room temperature. A sample of this oil is examined for acid and saponification numbers. The ester number obtained thereby represents lactones, but only to the extent that they are regenerated after saponification and re-acidification.

Although Lewkowitsch correctly stated in 1921 that "the free acid (i. e., gamma-hydroxystearic acid) has not been prepared yet (from stearolactone), for whenever the free acid may be expected its inner anhydride, or lactone, is formed (*25*)," nevertheless, in 1924 Clutterbuck (*4*) showed that pure stearolactone can be converted into a stable hydroxystearic acid, which can be isolated. Clutterbuck's experiment was confirmed in this laboratory with the additional discovery that, in the presence of the other naturally occurring constituents of the reaction mass, one cannot convert stearolactone into stable gamma-hydroxystearic acid. In other words, to repeat Clutterbuck's experiment successfully pure stearolactone must be employed. This is a probable reconciliation of Clutterbuck's discovery with Lewkowitsch's earlier statement, since the latter apparently did not use pure stearolactone, notwithstanding the rather obvious inference that he did attempt to obtain stable gamma-hydroxystearic acid from the pure lactone. Further experimentation in this laboratory indicates, oddly enough, that oleic acid, or 1–10 hydroxystearic acid, or a mixture of the two, does not prevent conversion of pure stearolactone into stable gamma-hydroxystearic acid.

The analyses of the pure stearolactone and pure gamma-hydroxystearic acid that were prepared are shown in Table XI.

Table XI—Constants of Stearolactone and Gamma-Hydroxystearic Acid as Prepared

	Stearolactone		γ-Hydroxystearic Acid	
	Found	Theoretical[a]	Found	Theoretical
Melting point	49° C.	...	76° C.	...
Acid number[a]	0.7	0.0	185.9	187.0
Saponification number	198.8	198.9	185.9	187.0
Ester number	198.1	198.9	0.0	0.0
Iodine number	0.5	0.0	0.2	0.0
Acetyl number	0.0	0.0	10.0	164.0
	99.5%	...	99.5	...

[a] The acid number of acetylated gamma-hydroxystearic acid was found to be only 37.0, indicating that the acetylation process had converted most of the gamma-hydroxystearic acid to stearolactone.

The previous data become more informative in view of the following experiment. A sample of an oleic acid sulfation, so washed and treated as to free it from sulfuric acid and fatty sulfates, and then saponified and acidified to destroy the ester acids, showed the following values:

Acid number	131.5
Saponification number	188.7
Ester number	57.2

This indicated 28.6 per cent stearolactone.

The above sample, after analysis, was re-saponified, re-acidified, and the material again analyzed. The constants were as follows:

Acid number	130.5
Saponification number	189.6
Ester number	59.1

This indicated 29.5 per cent stearolactone.

The identical procedure was repeated on the same sample. The third analysis was as follows:

Acid number	130.0
Saponification number	189.0
Ester number	59.0

This indicated 29.5 per cent stearolactone.

The above experiments proved that, in this reaction mass, acidification always converted the gamma-hydroxystearic acid to stearolactone.

The stearolactone was separated from the triple-saponified and triple-acidified reaction mass by neutralization of carboxylic hydrogen and extraction with petroleum ether. The acid number of the extract was zero. Saponification and acidification of this extracted stearolactone produced gamma-hydroxystearic acid, as indicated by the following analysis:

Acid number	183.8
Saponification number	198.0
Ester number	14.2
Probable amount stearolactone regenerated	7.1%
Probable amount γ-hydroxystearic acid generated	92.9%

When the saponification-acidification procedure is applied to castor oil products, the ester number will be found practically to disappear, indicating that lactones are either not present or that they are not regenerated spontaneously in the saponification and acidification.

The decrease in ester number on applying the saponification-acidification procedure represents anhydrides and ester acids, since these are not regenerated after being converted to simple fatty acids in the absence of heat.

Free Sulfur—The accepted method of determining "free sulfur"—i. e., sulfur present as sulfuric acid, or, in the case of neutralized oils, as sulfates—by washing an ethereal solution of the sample with saturated salt solution and precipitating the sulfate as barium sulfate (*23*) is accurate.

Water—Dean and Stark's distillation method is accurate (*5*). Toluene has been used to replace xylene. Drying in the oven is unsuitable, since the last traces of water are held tenaciously by a sulfated oil.

Acid Number and Saponification Number—The methods given by Lewkowitsch (*29*) were adopted as satisfactory. It must be remembered that an unneutralized sulfated oil contains sulfuric acid and sulfo acids as well as acids containing only carboxylic hydrogen, and therefore the acid

number and the saponification number will not have their usual significance. The difference between them, the ester number, does represent lactones, anhydrides, and poly-acids as limited above.

NEUTRAL FAT—The glycerol-ammonia extraction method (*15*) is not entirely satisfactory, inasmuch as the extract of supposedly neutral fat is sometimes emulsifiable with water, showing the presence of water-soluble matter. In some cases it has been found to contain the higher poly-acids, such as would be expected to show greater solubility in petroleum ether because of the relatively small proportion of carboxyl group present. It was the only method examined, however.

TOTAL FATTY MATTER—This figure may be found by boiling with mineral acid until the oil is bright, and then weighing the separated oil, after washing free from mineral acid in ethereal solution.

UNSAPONIFIABLE MATTER—The method of Allen and Thomson (*30*) has been used. Continued drying in the oven will produce a continuous loss in weight, and therefore it is recommended that drying be discontinued when the loss has been reduced to 0.1 to 0.2 per cent between weighings.

ASH—Determination of the ash in the finished product in the usual manner will detect the use of caustic soda or potash in the neutralization. For determining the proportion combined with the carboxyl group, see the section under "Ammonia."

Notes

An investigation of various methods for the determination of glycerol in sulfated oils is now being conducted in this laboratory. It is hoped that the results may be presented in a subsequent paper.

In this laboratory it has been found desirable to replace ethyl ether with isopropyl ether in many of the foregoing procedures. The latter has a higher boiling point, a lower vapor tension, dissolves less water, dissolves less readily in water, and has a smaller tendency to form troublesome emulsions in the presence of fatty materials and water.

Tables XII and XIII show typical analytical results obtained on sulfated oils.

Table XII—Typical Analytical Results on Sulfated Oils

Sample number	1	2	3	4	5	6
Total SO_3 (Parr bomb)	2.18	1.79	6.46	5.01	2.05	2.41
Total SO_3 (HCl-boiling)	1.86	1.06	6.43	5.05	0.49	1.17
Free SO_3	0.16	0.38	1.03	0.75	0.25	0.63
Combined SO_3 (from Parr bomb)	2.02	1.41	5.43	4.26	1.80	1.78
Combined SO_3 (from HCl-boiling)	1.70	0.68	5.40	4.30	0.24	0.54
Total ammonia	1.05	1.33	3.35	1.37[a]	...	2.95
Carboxyl ammonia	...	...	1.76	0.13[a]	1.41	...
Water	45.38	7.49	15.75	39.5	7.5	15.29
Ash	0.04	0.08	...	5.72	...	...
Unsaponifiable	0.37	6.00	...	0.44	34.8	...

[a] Caustic soda was actually used in this sample, as shown by the high ash. Titration results were calculated to per cent ammonia.

Table XIII—Typical Values for Constants of HCl-Boiled Fatty Matter from Sulfated Oils

Sample number	1	2	3	4	5	6
Acid number	117.5	72.5	141.5	115.5	128.0	101.2
Saponification number	185.0	192.4	201.0	197.2	198.3	186.5
Iodine number	80.9	66.0	74.5	60.9	38.1	66.6
Acetyl number	137.4	...	106.8	103.9	...	49.5
Hydroxyl number	...	71.9	...	...	26.1	...

Summary

It should be noted that the work of prior investigators has been confirmed as follows: sulfation of castor oil does take place, in part, at the double bond; a stable gamma-hydroxystearic acid is not obtainable from stearolactone without first separating the stearolactone from the accompanying fatty bodies.

The authors have shown that the ordinary water-soluble sulfoleic acid is essentially the 1–10 acid. The ordinary sulforicinoleic acid is, in part, an ester acid containing a non-sulfated ricinoleic acid residue. These acids are completely decomposed by sufficient boiling in the acid state. The use of the Parr peroxide bomb in determining total sulfur in sulfated oils gives a value which is an entirely new index of comparison and presents a new conception of the sulfur-containing elements in sulfated oils. The iodine numbers of fatty modifications should be determined by the Hübl-Waller method, although, under certain conditions, the Margosches method may be employed. The use of the acetyl number involves a correction sometimes ignored.

Other data have been included on composition, nomenclature, and analytical procedure.

Although determination of the actual constituents of a fatty modification is not always possible, and even though the identification of the parent oil is often difficult, one can always ascertain that modification has taken place.

Acknowledgment

Acknowledgment is made to the Department of Chemistry of the Washington University, St. Louis, Mo., for the investigation of the oxygen bomb method for total sulfur. The authors also wish to express their appreciation of the kindness of R. K. Brodie, of the Procter and Gamble Company; W. A. Hamor, of the Mellon Institute; A. Lowy, of the University of Pittsburgh; Leroy McMaster, of the Washington University; and W. C. Adams, Edward H. Keiser, and C. N. Stehr, of this laboratory, in reading the manuscript.

Literature Cited

(1) Bauer, *Chem. Umschau Fette, Oele, Wachse Harze*, **36**, 290 (1929).
(2) Bauer, *Ibid.*, **36**, 102 (1929).
(3) Benedikt, *J. Soc. Dyers Colourists*, **4**, 45 (1888).
(4) Clutterbuck, *J. Chem. Soc.*, **125**, 2330 (1924).
(5) Dean and Stark, Am. Soc. Testing Materials, Standard Method D95–28.
(6) Elsdon, "Edible Oils and Fats," p. 136, Van Nostrand, 1926.
(7) Gansel, *Chem. Umschau Fette, Oele, Wachse Harze*, **36**, 284 (1929).
(8) Griffin, IND. ENG. CHEM., Anal. Ed., **1**, 167 (1929).
(9) Hart, J. IND. ENG. CHEM., **9**, 850 (1917).
(10) Hart, *J. Am. Leather Chem. Assocn.*, **15**, 404 (1920).
(11) Hellmut-Gnamm, "Die Fettstoffe in der Lederindustrie," p. 454, Stuttgart, 1926.
(12) Herbig, *Seifensieder-Ztg.*, **55**, 134 (1928).
(13) Herbig, *Ibid.*, **55**, 427 (1928).
(14) Holde, "Hydrocarbon Oils and Saponifiable Fats and Waxes," p. 140, Wiley, 1922.
(15) Holde, *Ibid.*, p. 483.
(16) Hurst and Simmons, "Textile Soaps and Oils," p. 138, Scott, Greenwood, 1921.
(17) Juillard, *Bull. soc. chim.*, **11**, 280 (1894).
(18) Juillard, British Patent 17,655 (1909).
(19) Knecht, Rawson, and Loewenthal, "A Manual of Dyeing," Vol. II, p. 807, Griffin, 1925.
(20) Lang, IND. ENG. CHEM., **20**, 693 (1928).
(21) Lewkowitsch, "Oils, Fats, and Waxes," Vol. III, 6th ed., p. 212, MacMillan, 1923.
(22) Lewkowitsch, *Ibid.*, p. 210.
(23) Lewkowitsch, *Ibid.*, p. 213.
(24) Lewkowitsch, *Ibid.*, p. 214.
(25) Lewkowitsch, *Ibid.*, p. 231.
(26) Lewkowitsch, *Ibid.*, pp. 244–258.
(27) Lewkowitsch, *Ibid.*, Vol. I, p. 437, MacMillan, 1921.
(28) Lewkowitsch, *Ibid.*, p. 439.
(29) Lewkowitsch, *Ibid.*, pp. 446, 388.
(30) Lewkowitsch, *Ibid.*, p. 467.
(31) Margosches and Fuchs, *Z. angew. Chem.*, **40**, 778 (1927).
(32) Meigen and Winogradoff, *Ibid.*, **27**, 241 (1914).
(33) Nonaka, *Seifensieder-Ztg.*, **56**, 288 (1929).
(34) Peterson and West, *J. Biol. Chem.*, **74**, 379 (1927).
(35) Pickering, *J. Soc. Chem. Ind.*, **39**, 305T (1920).
(36) Richardson and Walton, *Ibid.*, **31**, 105 (1912).
(37) Riess, *Chem. Umschau Fette, Oele, Wachse Harze*, **36**, 77 (1929).
(38) Rosenmund and Kuhnhenn, *Z. Nahr. Genussm.*, **46**, 154 (1923).
(39) Schmitz and Tönges, German Patents 60,579 (Dec. 22, 1891); 64,073 (July 23, 1892).
(40) Tomecko and Adams, *J. Am. Chem. Soc.*, **49**, 522 (1927).
(41) Twitchell, *J. Soc. Chem. Ind.*, **16**, 1003 (1897).
(42) Twitchell, U. S. Patent 601,603 (March 29, 1898).
(43) Twitchell, *J. Soc. Chem. Ind.*, **36**, 179 (1917).
(44) Verley and Bölsing, *Ber.*, **34**, 3354 (1901).
(45) Welwart, *Chem.-Ztg.*, **44**, 719 (1920).

The Chemistry of Wood—III

Part 1—Comparison of Two Methods for Determination of Lignin[1]

Louis E. Wise and A. M. Fairbrother

New York State College of Forestry, Syracuse University, Syracuse, N. Y.

THE lignin determination which has always rested on highly arbitrary procedures, has ordinarily involved the removal, by solution and hydrolysis, of the polysaccharides by means of acids, and the weighing of a partially degraded residue (*2*). Investigators have never deluded themselves with the idea that this residue was identical with the genuine lignin as it occurs in the cell walls, but at least they have been able to obtain reproducible fractions of material which were reasonably free from carbohydrates. One of the most satisfactory methods involving this procedure for lignin is that of the U. S. Forest Products Laboratory. Very recently, Ross and Hill (*3*) have devised a method which is based on the solution of lignin as well as that of the polysaccharides of the cell wall. Lignin in the presence of formaldehyde is readily peptized by sulfuric acid, and may then be reprecipitated by pouring the solution into water. In the following report, the results obtained by the Ross-Hill method, which has the merit of being simple and rapid, have been compared with those obtained by using the procedure of the Forest Products Laboratory. The lignin content of thirteen common woods was determined by these two methods, and slight but convenient changes in the technic of either method have been described.

Experimental Procedure

The air-dried wood samples were carefully reduced to sawdust by holding a rasp against the wood while it was turned on a lathe. This sawdust was sifted and that which passed an 80-mesh screen, but was retained on a 100-mesh screen, was used for analysis.

Moisture determinations were made by drying at 105° C., and extractives were determined by using a mixture of equal volumes of ethanol and benzene and extracting the air-dried wood. It was found expedient to extract sufficient material (ordinarily 5 to 10 grams) in one operation, so that duplicate lignin determinations on the extracted wood could be made using either method. In the case of two woods, chestnut and oak, which are rather high in water-soluble matter, the alcohol-benzene extraction was preceded by a hot water extraction. Lignin determinations were made on this extracted material, but the results were always calculated on the oven-dry basis of the original wood.

Determinations by Procedure of Forest Products Laboratory

This method, which has recently been fully described (*1*), was employed with the following modifications: One-gram samples of dried, extracted material were used and the acid hydrolysis (with 20 cc. of 72 per cent sulfuric acid) was carried out in 100-cc. Erlenmeyer flasks fitted with one-hole stoppers, in which were inserted glass stirring rods, 15 cm. long and flattened at the end so that lumps of sawdust could be conveniently broken up. These flasks were kept cool during the first hour, and the mixtures were thoroughly stirred at 5-minute intervals during the first three-quarters of an hour. At the end of 16 hours the mixture was transferred to a liter wide-mouth Erlenmeyer flask, diluted to 875 cc. with water, and boiled under a reflux for 2 hours. A simplified condenser, which proved very satisfactory, consisted of a copper cap fitting over the mouth of the flask, and provided with a small lead pipe, whose ends protruded through the cap at an angle of 180 degrees, and which formed a spiral coil that extended about 2 inches (5.08 cm.) into the neck of the flask. Condensing water was passed through this lead pipe, and condensers of this type could be set up rapidly and conveniently in series.

The lignin was filtered on balanced filters, instead of resorting to the usual filtration by suction. Balanced quantitative filter papers (11 cm.) were folded and placed one inside the other in a 7-cm. funnel. The supernatant liquid was siphoned into these funnels by means of glass and rubber tubing with a clamp governing the rate of flow. When once adjusted, this apparatus was continuous. After the clear liquid had been filtered, the precipitate was poured into the filter and the flask washed free from lignin particles without difficulty.

The lignin residue was washed with hot water until the filtrate failed to give a test for sulfates with barium chloride. The balanced filters were then dried overnight at 100° C.

By this method of filtering it was possible ordinarily to transfer the precipitate on the filter and to wash it, in approximately 1 hour. In the case of several coniferous woods, the filtration was complete in one-half hour. Hardwood lignin appeared to be much more gelatinous and was more difficult to wash. Even the most obstinate residue could be filtered and washed in 2 hours.

It was observed that the filtrate and washings from the coniferous lignin were colorless, while those from the hardwoods were amber in color. After drying, the funnels containing the residues were removed from the oven and allowed to cool in a desiccator. The paired filter papers in each funnel were then cautiously removed with forceps and separated from each other. The weighing was made in each case with the upper filter containing the lignin on one pan of the balance and the paired filter on the other. The amount of lignin was then determined directly by the usual method of weighing.

This technic for filtering and weighing lignin has been used for several years in this laboratory, and has been found more generally satisfactory than that involving the use of an alundum crucible.

Determination by Ross-Hill Method

This method, involving the use of formaldehyde followed by concentrated sulfuric acid, was employed as originally described (*3*), but a modified procedure was adopted in the collection and the weighing of the lignin precipitate.

The filtration and washing of this precipitate presented a real problem. Ross and Hill accomplish this filtration by adding a suspension of asbestos to the mixture and filtering on a Gooch crucible and refiltering until the solution is freed from the precipitate. The precipitate is then washed with 250 cc. of 5 per cent hydrochloric acid.

Although the filtration was found possible, the washing required several hours and great care was necessary in order not to disturb the filtering mat and thus necessitate re-

[1] Received February 5, 1931. Presented before the Division of Cellulose Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

filtration. It was preferable, therefore, to adopt some other method for the collection of the isolated lignin. The use of alundum and Jena glass crucibles was tried, but the particles were drawn through the small openings which eventually became so tightly plugged that further filtration was impracticable. The balanced filter method also proved inexpedient, since the procedure called for final washing with hydrochloric acid and not with water, and this involved partial hydrolysis of the cellulose.

The use of a centrifuge was suggested and this was found to be a rapid and satisfactory means of washing and collecting the precipitate for weighing. The centrifuge used for this purpose was run by a small universal motor at a speed of 3500 r. p. m. It was equipped with removable heads accommodating cups and tubes of different sizes. The largest cups could accommodate wide-mouth bottles of convenient size, which were filled from the beakers in which the lignin precipitation had been made. After centrifuging again for 10 minutes, the lignin residue separated in a compact layer, and the supernatant liquid could be removed sharply by gentle suction, using a tube fitted to a suction flask. To obviate the hazard of drawing precipitate as well as liquid out of the centrifuge cup, this tube was sealed at the tip, and had an opening on its side about $^1/_8$ inch (0.31 cm.) from this tip. Thus if the tip were accidentally brought into contact with the precipitate, the tube would draw off liquid without disturbing the lignin layer, and when the liquid was exhausted, air would be sucked through the tube.

The lignin residue was washed repeatedly with 5 per cent hydrochloric acid, centrifuged, and the liquid siphoned off, using the above-mentioned technic. This type of washing was resorted to until the supernatant liquid was free from sulfates. In our experience this required about 500 cc. of 5 per cent hydrochloric acid and could not be obtained with 200 cc. as suggested by Ross and Hill. After the final washing, the liquid was removed as completely as possible, the precipitate was loosened from the bottom of the bottle with a policeman, and a thin suspension made by the addition of 5 per cent hydrochloric acid. This was transferred, in convenient portions, to a weighed centrifuge tube of 15 cc. capacity, and centrifuging was again resorted to in separating the lignin. The supernatant liquid was again removed by suction. The tube and lignin were then dried to constant weight at 105° C. The incineration, suggested by Ross and Hill, was not carried out, since we wished to obtain results comparable with those obtained by the Forest Products Laboratory procedure.

The results are given in Table I. The data are in fair agreement, when we consider the differences in procedure. As previously noted by Ross and Hill, the lignin fraction from hardwoods is uniformly higher when the Forest Products method is employed. Strangely enough, in the case of chestnut and oakwood, hot water extraction followed by alcohol-benzene pretreatment gives a material which when analyzed by either method yielded rather similar results. This agreement (in which there is a difference of less than 1 per cent between the data furnished by the U. S. and the Canadian methods) suggests that possibly by the use of other mild solvents, prior to the lignin determination, more concordant results may be expected.

It is interesting to note also that in the case of all the coniferous woods studied, the Ross-Hill method gave the higher results and that the greatest discrepancies are found here. Whether or not these higher figures are due to condensation products between formaldehyde and a lignin which characterized the conifers (in contradistinction to hardwood lignin), or whether due to imperfectly hydrolyzed and partially reprecipitated polysaccharides, or possibly to incomplete extraction of extraneous components of wood, cannot be answered at present. Of the two procedures, the Ross-Hill method is far more rapid and somewhat more convenient, since the initial solution and hydrolysis require very little time, as compared with the long initial hydrolysis demanded by the Forest Products Laboratory method. The usefulness and simplicity of the Ross-Hill method warrants its further critical study, and the use of solvents other than alcohol-benzene is suggested.

Table I—Lignin Data

(Percentage based on oven-dried, unextracted wood)

Species	Extractives Based on Oven-Dried Wood	Lignin by Forest Products Lab. Method	Lignin by Ross-Hill Method	Difference (Av.)[a]
	%	%	%	
Sugar maple (*Acer saccharum*)	2.16	24.06 24.00	21.68 22.11	−2 64
Yellow birch (*Betula lutea*)	2.68	20.60 20.57	18.22 17.82	−2.06
Chestnut (*Castanea dentata*)	6.34	23.75 23.65	22.81 22.80	−0.9
Beech (*Fagus grandifolia*)	0.97	22.57 22.20	19.98 19.56	−2.62
Popular (*Populus grandidentata*)	2.89	19.91 20.29	16.54 16.52	−3.07
White oak (*Quercus alba*)	6.57	24.35 24.25	23.52 23.51	−0.78
American elm (*Ulmus americana*)	0.97	26.19 26.19	23.61 23.56	−2.61
White spruce (*Picea glauca*)	1.55	26.54 26.51	27.47 27.68	+1.05
Longleaf pine (*Pinus palustris*)	5.50	24.60 24.85	30.05 30.33	5.79
N. white pine (*Pinus strobus*)	4.36	26.15 26.10	28.77 28.77	2.65
Sugar pine (*Pinus lambertiana*)	5.99	28.24 27.76	31.62 31.72	3.67
Eastern hemlock (*Tsuga canadensis*)	1.61	29.27 29.23	31.18 31.12	1.90
Redwood (*Sequoia sempervirens*)	6.98	33.58 33.61	36.65 36.56	3.01

[a] Minus sign indicates that the results by the Forest Products Laboratory method are higher, and plus sign indicates that they are lower.

Part 2—Comparison of Two Methods for Preparation of Lignin from Wood

William M. Harlow and Louis E. Wise

AS ALREADY indicated in Part 1, the Forest Products Laboratory's technic of filtration using a porous alundum crucible in collecting the lignin has been modified here by the substitution of matched filters. It was found that time could be saved at the start, since the counterbalancing of filter papers requires less time than the bringing of an alundum crucible to constant weight. In addition, especially in the case of hardwood lignin which tends to slow up filtration by plugging the pores of the crucible, time could be saved in the washing of the residue. A final slight advantage was the fact that the lignin could be weighed directly on the balance, using the paired filter as a counterpoise.

Since some trouble has been experienced in the industry in securing comparable results on portions of the same sample by these two methods, it seemed advisable to check them against each other. The procedure was the same as that outlined in Part 1 except that the percentages given in Table

II are computed on the alcohol-benzene extractive-free basis. The wood acid mixture was diluted according to the Forest Products Laboratory's technic (*1*) and, after refluxing and settling, the supernatant liquid and residue were transferred directly to the crucibles and filter papers. The yields of lignin recorded in Table II indicate that the two methods of filtration give comparable results when applied to the same sample, and that hence either may be used as convenience dictates.

Table II—Lignin from Same Sample Using Two Different Methods of Filtration

Species	Lignin by Forest Products Lab. Method	Lignin by Matched Filter Paper Method
	%	%
Beech (*Fagus grandifolia* Ehrh.)	26.08 26.50	25.85 25.70
Basswood (*Tilia glabra* Vent.)	20.10 20.13	20.44 20.70
Red spruce (*Picea rubra* Link.)	28.38 28.36	28.54 .....
White pine (*Pinus strobus* L.)	27.95 27.91	27.99 27.93

Literature Cited

(1) Bray, *Paper Trade J.*, **87**, No. 25, 59 (1928).
(2) Fuchs, "Die Chemie des Lignins," p. 69, Springer, 1926.
(3) Ross and Hill, *Pulp Paper Mag. Can.*, **27**, 541 (1929).

Moisture Content of Liquid Sulfur Dioxide[1]

A. K. Scribner

Virginia Smelting Company, West Norfolk, Va.

THE ever-increasing use of liquid sulfur dioxide by the electrical refrigeration industry has created wide interest in suitable methods for determining the traces of moisture found in this product. The procedure to be described is rapid, uses a minimum sample, will produce consistent results in any laboratory, and has been in actual plant control work for several years.

The specifications for liquid sulfur dioxide suitable for refrigeration once called for moisture below 200 p. p. m. but today all manufacturing guarantees are below 50, and the actual water content will reach 5 p. p. m. in much of the material shipped. The total evaporation of 146 grams of sulfur dioxide containing 200 p. p. m. of water leaves a residue visible but difficult to estimate. Above this point the water residue increases steadily and can be measured in the tips of the tubes shown in Figure 1.

Table I contains data on the fractionation of wet sulfur dioxide boiling at normal pressure and temperature and furnishes a basis for determining the total moisture content of this sulfur dioxide. (Evaporate a 146-gram sample, record the residue, and refer to Table I.)

Table I—Fractionation of Boiling Sulfur Dioxide[a]
(Sample of sulfur dioxide taken, 146 grams)

(*A*) Moisture as Residue on Evaporation	(*B*) Moisture as Residue Figured on Sample[b]	(*C*) Moisture Figured on P_2O_5 Gain on Evaporation	(*D*) Total Moisture
Ml.	%	%	%
0.005	0.003	0.022	0.025
0.010	0.007	0.023	0.030
0.015	0.010	0.024	0.034
0.020	0.013	0.025	0.038
0.04	0.027	0.027	0.054
0.06	0.040	0.030	0.070
0.08	0.053	0.034	0.087
0.10	0.067	0.038	0.105
0.40	0.267	0.070	0.337

$$\frac{A \times 1}{146} + \frac{P_2O_5 \text{ gain in grams}}{146} \times 100 = \text{total \% moisture}$$

or

$$B + C = D$$

[a] Water above 250 p. p. m.
[b] $\frac{A \times 1}{146} \times 100 = B$.

The inability to see residual water in the moisture tubes has often led to the statement that the sulfur dioxide in question was anhydrous. Chemical tests indicate that this liquid sulfur dioxide contains water, but that the amount of water going off with the sulfur dioxide vapor phase is an increasingly large percentage of the total water. The residue is difficult to determine, but its presence can be detected by the use of the blade test.

A bright piece of low-carbon Swedish steel placed in a sample of boiling sulfur dioxide of 200 p. p. m. water content remains bright during the evaporation, and does not tarnish until the last traces of liquid sulfur dioxide are evaporated. At this point, the blade gives evidence of considerable corrosion, pointing to a concentrated sulfurous acid, which we know is intensely active. The intensity of corrosion, as shown by the etching of the steel, decreases to a point at which the regular P_2O_5 analysis gives 65 p. p. m. Below this point the steel remains bright throughout the entire test.

This test is useful for non-quantitative reports of moisture stating that the sulfur dioxide contains "more than," or "less than" 65 p. p. m. of water.

Possible Methods

An actual determination of the water below 65 p. p. m. calls for an accurate method. Several have been tried.

The specific conductance of the liquid phase can be determined and specifications written on this basis, but the test is difficult and has not yet been developed for practical use in plant control work.

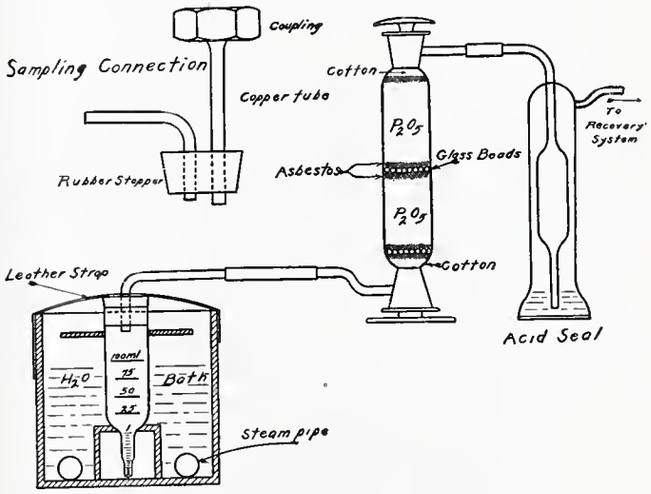


Figure 1—Apparatus for Moisture Determination

An Engelhard cell was used in an endeavor to obtain a moisture curve from the differences in the thermal conductivity of the vapor phase rising from a boiling sample of sulfur dioxide. This method failed.

The color change of a chemical added to boiling sulfur

[1] Received February 6, 1931.

dioxide would be the ideal procedure, but up to the present time nothing worth while has been developed.

Rapid evaporation of samples with the vapor passing over desiccating agents such as anhydrone, dehydrite, and especially prepared aluminum oxide, was unsatisfactory. Phosphorus pentoxide proved to be the only satisfactory desiccating agent, and is the one now used in this laboratory.

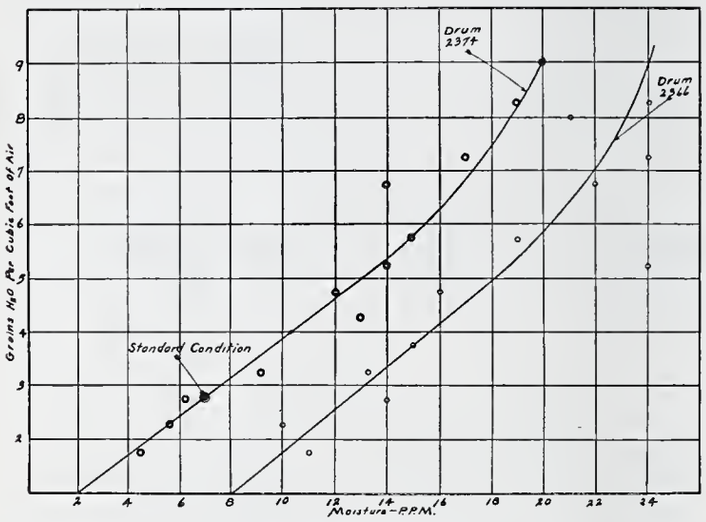


Figure 2—Barometer Drum Tests *vs.* Grains of Water per Cubic Foot of Air

The following method for plant control work is based on a demand for reliable data within $1^1/_2$ hours after the sample is taken, and a production of 100 or more analyses daily.

Equipment

The equipment consists of copper sampling connections, especially built Fleming jars packed with P_2O_5-asbestos mixtures, sulfuric acid guide bottles or seals, and moisture tubes graduated as shown in Figure 1. These tubes have a volumetric capacity of 200 ml., but the sulfur dioxide sample consists of 100 ml. or 146 grams.

Procedure

The samples originate from the plant and from shipping containers which have a variable capacity of from 5 to 40,000 pounds (2.27 to 18,144 kg.). Each container is tested. Groups of ten samples are usually taken, and transported in an insulated box to the laboratory, the sulfur dioxide being at 14° F. (−10° C.).

Before sampling, 10 Fleming P_2O_5 jars, already in service, are standardized by the passage of 50 grams of sulfur dioxide. Freshly packed jars should always be standardized by the passage of 500 ml. of sulfur dioxide gas. Before closing the stopcocks, the jars are vented to the air for 3 seconds, because the speed of evaporation may build up as high as 4 inches (10.16 cm.) of mercury pressure.

At the time of closing the stopcocks, the temperature humidity, and barometer are always recorded. The jars are wiped by passing a dry cloth over them gently, and then weighed, using calibrated weights. The jars are now placed in their racks, ready for the test.

The sample to be analyzed is drawn into a dry, clean moisture tube through the special copper connection. Before sampling, the container valve is blown off, and is then dried, with its sampling device, by a blow torch. The withdrawal of 146 grams of sulfur dioxide requires a few seconds, but the total used for a double check test averages $1^1/_2$ pounds (0.680 kg.) per container.

The moisture tubes on reaching the laboratory are hooked up one by one to the closed P_2O_5 jars. This is possible because the sulfur dioxide at 14° F. (−10° C.) in the frosted moisture tubes creates almost no pressure. As each moisture tube is placed on the line, the bottom and top stopcocks of the jars are successively opened, and the rate of flow is measured by bubble formation in the acid seal.

The vapor formation and duration of the tests are controlled by a water bath. The sulfur dioxide flow is maintained at a constant rate during the 60-minute period of the test by gradually elevating the temperature of the water bath as the evaporation proceeds. Leather straps hold the stoppers in the moisture tubes.

On completion of the evaporation, the jars are brought to atmospheric pressure and closed. All conditions are recorded, the jars are wiped in exactly the same manner as before, weighed, and placed in position for the next test that follows immediately.

Moisture tubes are also checked for residue, but sulfur dioxide suitable for refrigeration is water-white, and should leave no residue, oil, or water on evaporation.

Proximate Calculation

$$\frac{\text{Grams gain by } P_2O_5}{146} \times 100 = \%\ H_2O \text{ in } SO_2;\ \text{all conditions constant}$$

Correction for temperature change during test period:
- Add 1.3 p. p. m. for each ° F. rise
- Subtract 1.3 p. p. m. for each ° F. fall

Correction for barometer change during test period:
- Add 1 p. p. m. for each mm. rise
- Subtract 1 p. p. m. for each mm. fall

Discussion

The correction factors just described are important and will be explained in more detail, because in this work our average P_2O_5 gain is small. On a 10 p. p. m. average the gain is only 15 mg. on the 146-gram sample.

The Fleming jars, when properly packed with the P_2O_5 asbestos and beads, have voids equivalent to 59 per cent of their total cubical content, which is 0.1025 gram of sulfur dioxide. A difference in temperature between the start and finish of the test will vary this sulfur dioxide content of the P_2O_5 jar enough to influence results. In fact, a variation of 1° F. will give an error in analysis of 1.3 p. p. m.

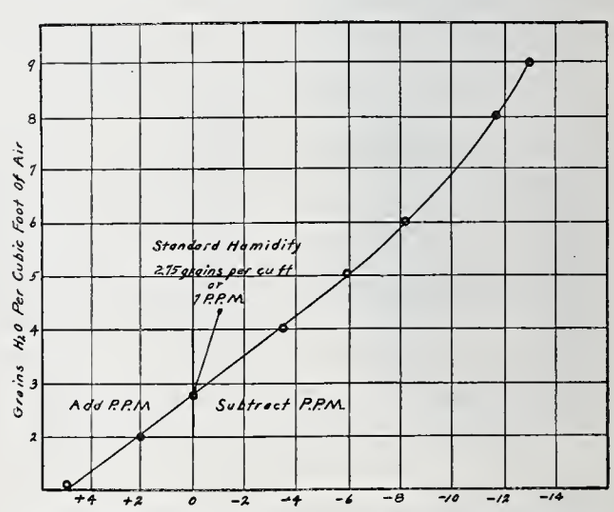


Figure 3—Correction Curve for Standard Conditions

It is difficult in most laboratories to have constant temperature, so the above adjustment should be made for temperature changes.

The inlet and outlet tubes on the standard P_2O_5 jars have a volumetric capacity of 1 ml., which is 0.0029 gram of sulfur dioxide. If the sulfur dioxide is replaced by air, the loss in weight would be 0.0016 gram, or an error of 10 p. p. m. in the

test. Therefore, all jars not air-flushed should be weighed quickly after the test. Standing in desiccators will cause deviations, and to avoid this, the jars used call for inlet and outlet capacities of only 0.25 ml.

Barometric changes will affect ultimate results. For instance, a rise or fall of 10 mm. will give a change of 0.0015 gram in the sulfur dioxide capacity of the jar. This is 10 p. p. m., or 100 per cent error. By working in a 60-minute period, deviations from this source are avoided.

Large samples of 500 to 1500 grams of sulfur dioxide evaporated over periods of 5 to 24 hours checked the 60-minute samples within 15 per cent, thus justifying the use of a quick method for control work.

Moisture tubes and other sampling flasks were flushed with dry sulfur dioxide, washed with liquid sulfur dioxide, and then used for the analytical sample. In these cases, the results checked standard analyses taken when the moisture tubes were merely wiped carefully with a warm cloth and kept in an oven between tests.

Blank Test

Variations in analyses made at different seasons of the year and by widely scattered laboratories led to a daily test of one 2000-pound (907-kg.) container called the barometer drum. The actual moisture content of this liquid sulfur dioxide could not alter, but the moisture content as reported by the laboratory varied from time to time. In warm weather, the apparent p. p. m. rose, but on cool, dry days, they decreased. This variation in moisture content was always accompanied by an atmospheric change—namely, the grains of moisture per cubic foot of air. The maximum average month at West Norfolk was June, with 7.5 grains, and the minimum average was December, with 2.5 grains. The daily maximum was 9, and the daily minimum was 0.6.

For 18 months, tests were made on this so-called barometer drum, or blank. The results figured in p. p. m. were plotted against the grains of moisture per cubic foot of air, and produced the curve shown in Figure 2. Several hundred subsequent tests have checked the correctness of this curve as applied to the analytical procedure just described.

The adjustment of all tests to standard conditions is made easy by the correction curve, Figure 3. This is based on a standard of 2.75 grains and 7 p. p. m. for the blank test. The moisture content of samples taken in groups with the blank reflect the variations shown by Figures 2 and 3. Therefore, any test with known humidity can be corrected to standard conditions. When the grains are above 2.75, a minus correction in p. p. m. is applied to the proximate analysis. Below 2.75, a plus correction is used.

Ultimate Calculation

P. p. m. in proximate analysis ± p. p. m. correction = ultimate analysis

Example—Proximate result	=	15 p. p. m.
Grains per cu. ft.	=	4.55
Correction	=	−5
Ultimate analysis	=	10 p. p. m.

Conclusion

Elaborate equipment and methods of analysis with absolutely constant conditions the entire year should enable one to obtain check tests day by day. Small laboratories interested in the moisture content of sulfur dioxide do not have the facilities, the extensive technical control, and the equipment for this work. They can, however, follow the method just described and use the correction curve shown in Figure 3 to place their results on a standard basis for comparison.

Acknowledgment

W. F. Pond, M. L. Harris, and B. E. Yaffey, of the staff of this laboratory, assisted in the development and perfection of this method.

Quantitative Separation of Copper and Cadmium by Reduction of Their Salts with Potassium Formate[1,2]

Ellis I. Fulmer

Department of Chemistry, Iowa State College, Ames, Iowa

THIS work grew from observations upon the effect of heat on the formates of several metals. Copper formate when heated gave off metallic copper in such a state of subdivision that the metal came from the mouth of the test tube in a heavy copper-colored vapor. Lead formate yielded metallic lead; zinc formate, the oxide; cadmium formate, the metal and some carbonate. It was very apparent that the temperatures required for these reductions varied greatly with the metal concerned. Hence experiments were instituted to apply this temperature differential to the separation of copper and cadmium.

The heating of the formates of these metals for $2^1/_2$ hours at 150° C. effected a separation. However, this did not constitute a satisfactory quantitative method because of the powdery nature of the copper and the presence of varying amounts of cuprous carbonate formed.

The next reagent studied was sodium formate. The solution of the sulfates of copper and cadmium was made acid with formic acid and about 15 grams of sodium formate were added to each sample and the solution evaporated to dryness. The samples were placed in an oven at 130° C. for 1 hour. The residue, after cooling, was extracted with hot water. The undissolved material consisted of a mixture of metallic copper and cuprous carbonate. The filtrate was free from copper and an analysis showed all the cadmium to be present in the filtrate. The filtrate was evaporated to dryness and again placed in the oven. There was no reduction of cadmium salt until 145° C. had been reached.

Experiments with potassium formate showed several differences between this reagent and the sodium salt, which may be summarized as follows:

Reagent	Mixture Fuses °C.	Copper Salt Reduced °C.	Cadmium Salt Reduced °C.
Sodium formate	250	135 to 140	145 to 150
Potassium formate	150	100	200

[1] Received February 7, 1931.

[2] This material is taken from a thesis submitted by the author for the degree of master of arts at the University of Nebraska in 1913. The author feels that the material here summarized is interesting not only for the separation involved but in calling special attention to potassium formate as a reagent of more general applicability. Permission has been given by F. W. Upson of the University of Nebraska for the publication of the material in its present form. The author wishes to thank Benton W. Dales for advice during the progress of the work.

Moreover, the reduction of the copper salt with sodium formate gave a mixture of the metal and cuprous carbonate, whereas the reduction with potassium formate yielded the metal only in a spongy form. By means of this reagent, metallic copper was obtained from the sulfate, chloride, carbonate, nitrate, and fluoride. In the latter instance the beaker was etched by the hydrofluoric acid formed. The metals cadmium, cobalt, nickel, silver, and mercury were obtained by the same means.

For quantitative tests of potassium formate as reductant, the same procedure was used as above except that potassium formate was substituted, 15 grams of the reagent being added for each 2 grams of the sample. The solutions were evaporated on a hot plate until metallic copper began to separate out. The samples were then placed in the oven at 155° to 160° C. for $1^1/_2$ hours. When cooled, the residues were extracted with hot water and filtered through weighed Gooch crucibles. The metallic copper was washed with hot water and then with alcohol and ether. The crucibles were dried for a short time at 75° C. and the residue weighed as metallic copper. Since the copper is in a spongy form, care must be taken to avoid oxidation. The cadmium in the filtrate was determined by the usual method of igniting the carbonate to the oxide. Results of typical analyses are given in Table I.

Table I—Results of Reducing with Potassium Formate

Weight of $CuSO_4.5H_2O$	Copper by Reduction		Copper by Electrolysis
Grams	*Gram*	%	%
1.0658	0.2654	24.90	24.93
0.8750	0.2180	24.92	24.93
1.1147	0.2778	24.92	24.93
0.8474	0.2112	24.92	24.93

Volumetric Determination of Chromium and Nickel in Same Solution[1]

L. H. James

Reo Motor Car Company, Lansing, Mich.

THE following procedure, which is nothing more than the combination of a comparatively new method for the determination of chromium with the well-known method of Moore as modified by Johnson (*1*) for the estimation of nickel, was made possible only by the discovery of Willard and Cake (*3*) that boiling concentrated perchloric acid would oxidize compounds of chromium. The facility with which these two methods can be combined so that both chromium and nickel can be determined in the same solution, compensates at least in part in both time and material for the additional expense involved in the use of perchloric acid for the routine analysis of chrome-nickel alloys. The method for nickel, however, cannot be used successfully if either copper or cobalt is present in appreciable quantities, as both metals interfere in the cyanide titration of nickel.

Silicon is precipitated by boiling perchloric acid and can be readily and accurately determined along with the chromium and nickel if the method as given for nickel-chromium iron is used. It is advisable, however, after first removing the filtrate obtained by washing with dilute perchloric acid, from the suction flask for the determination of chromium and nickel, to wash the silica on the filter again with hot dilute hydrochloric acid and water before finishing the determination in the usual manner. Otherwise it is ordinarily necessary to volatilize the ignited silica with hydrofluoric acid in order to obtain accurate results. The end point of the nickel titration is also more easily detected after boiling with perchloric acid, as the solution is both clearer and lighter colored than is the case if this determination is carried out in the usual manner.

The procedure described for nickel-chromium iron is objectionable, as the results obtained are low because the silica retains small quantities of chromium and nickel if washed only with perchloric acid. The tendency for this method to give low results may also be increased by the possibility that the chromium is not entirely oxidized unless the graphitic carbon is totally removed by boiling with an excess of perchloric acid, and even if completely oxidized it may be reduced by the paper pulp used as a filtering medium. The results obtained by this method are not sufficiently low, however, to effect its usefulness seriously as a routine procedure.

[1] Received February 12, 1931.

More accurate results can be obtained if the following method for nickel-chromium iron is so modified that the chromium is titrated before the silica is removed by filtration. The silica can then be filtered out and washed with hot dilute hydrochloric acid and water before titrating the nickel. If the method is modified in this manner it is necessary to boil off the chlorine in the presence of the insoluble silica, a condition under which the solution has a tendency to bump rather violently. This inclination to bump is avoided in the proposed method, as the silica which causes this trouble is removed before boiling off the chlorine, a procedure which is thought to be the most desirable for routine work even though the results obtained are not quite so accurate as can be obtained by removing the silicon after first titrating for chromium.

Method for Chrome-Nickel and Stainless Steel

Chromium—Weigh 1 gram of chrome-nickel or 0.2 gram of stainless steel into a 500-cc. tall-form beaker and add 20 cc. of an acid mixture containing 250 cc. of nitric acid (sp. gr. 1.42), 750 cc. of hydrochloric acid (sp. gr. 1.19), and 1000 cc. of water. Heat until dissolved and add 20 cc. of perchloric acid (60 per cent). Boil until the perchloric acid fumes and the solution clears up and changes color. Continue to boil for 10 minutes after this change has taken place, cool, add 100 cc. of water, boil for 2 minutes, and cool. Add 25 cc. of sulfuric acid (sp. gr. 1.22) and an excess of 0.1 N ferrous sulfate. Titrate back with 0.1 N potassium permanganate to a permanent pink end point.

The chromium is calculated by means of the following formula which includes a titration correction of 0.2 cc. of 0.1 N potassium permanganate.

$$\text{Per cent chromium} = \frac{[(A \times B) - c + 0.2] \times 0.174 \times D}{\text{Weight of sample}}$$

A = cc. of 0.1 N ferrous sulfate
B = permanganate solution equivalent to 0.1 N sulfate
C = cc. of 0.1 N potassium permanganate
D = normality factory of 0.1 N potassium permanganate

Nickel—Add 50 cc. of citric acid solution and 110 cc. of ammonium hydroxide (sp. gr. 0.94) to the solution used for the determination of chromium. The citric acid solution is made by dissolving 500 grams of citric acid in 600 cc. of water and then diluting with 200 cc. of hydrochloric acid (sp. gr.

1.19). Cool, add 3 cc. of 0.0344 N silver nitrate, and then add ammonium hydroxide (sp. gr. 0.90) from a buret until the precipitate formed is just dissolved and the solution is clear. If the solution is warm at this point, cool again before titrating. Now add 10 cc. of potassium iodide (4 per cent solution in water), dissolve the precipitate with an excess of 0.0344 N potassium cyanide, and titrate back with 0.0344 N silver nitrate until one drop produces a permanent white turbidity.

The silver nitrate solution equivalent to the 0.0344 N potassium cyanide solution is obtained by titration in the same solution in which the nickel was determined. The 0.0344 N silver nitrate is standardized by the method of Mohr (*2*) against a 0.0344 N solution of sodium chloride.

The nickel is calculated by the following formula:

$$\text{Per cent nickel} = \frac{(A \times B) - c \times 0.1 \times D}{\text{Weight of sample}}$$

A = cc. of 0.0344 N potassium cyanide
B = nitrate equivalent of 0.0344 N cyanide
C = cc. of 0.0344 N silver nitrate
D = normality factor of 0.0344 N silver nitrate

Method for Nickel-Chromium Iron

Dissolve a 1-gram sample in a 500-cc. tall-form beaker with the same solution as used for steel, add 30 cc. of perchloric acid (60 per cent), boil until the fumes given off are white rather than yellowish in color, and then continue to boil quite vigorously for 20 minutes. Cool, add 50 cc. of water, filter on paper pulp with suction, and wash with a 1 per cent solution of perchloric acid. Determine the chromium and nickel in the filtrate as described in the method for steel.

The accuracy of the results expected with the above procedure are shown in Tables I and II in which are tabulated determinations for chromium and nickel for B. S. chrome-nickel 32, B. S. nickel-chromium iron 82, and stainless steel No. 1 which was standardized by the procedures ordinarily used for this purpose.

Table I—Chromium Determinations

Sample	Chromium Obtained 1	2	3	4	Av.	Chromium Present
	%	%	%	%	%	%
32a	0.87	0.88	0.86	0.87	0.87	0.88
82	0.21	0.23	0.20	0.22	0.21	0.24
1	7.66	7.57	7.48	7.57	7.57	7.63

Table II—Nickel Determinations

Sample	Nickel Obtained 1	2	3	4	Av.	Nickel Present
	%	%	%	%	%	%
32a	1.57	1.60	1.58	1.54	1.57	1.57
82	0.98	0.96	1.00	0.96	0.98	1.00
1	22.40	22.00	22.40	22.50	22.32	22.27

Literature Cited

(1) Lord and Demorest, "Metallurgical Analysis," 1913.
(2) Treadwell and Hall, "Analytical Chemistry," Vol. II, Wiley, 1915.
(3) Willard and Cake, J. Ind. Eng. Chem., **11**, 480 (1919).

A Modified Vacuum Regulator[1]

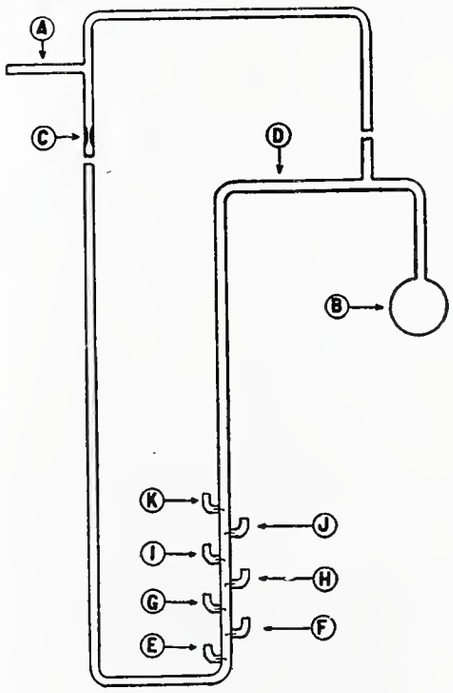
Arthur A. Sunier and Chester M. White

University of Rochester, Rochester, N. Y.

THE vacuum regulator described herewith, which is a modification of one described by Cox (*1*), has been found especially useful when a set of predetermined pressures are to be maintained in rotation in a given apparatus. The figure shows the regulator before filling with mercury. By tilting it, about 15 cc. of pure mercury are introduced through A into flask B (about 100 cc. capacity). The apparatus is then firmly clamped in an upright position with the mercury container resting on a sand bath. A Hyvac oil pump is attached at A by a three-way stopcock. During evacuation the entire apparatus is strongly flamed for an hour. Then mercury is slowly distilled into the manometer. When the mercury stands at about 39 cm. in both arms, the barometer tube is sealed off at the constriction, C. After air has been admitted through A, the distillation apparatus can be cut off at some point on D. This method of filling the manometer, which was suggested by Weatherill (*2*), has been found very satisfactory.

The side tubes with sealed-in lengths of tungsten wire (No. 24 B. and S.) are filled with mercury. The position of each has been calculated to correspond approximately to some desired pressure—thus F, 700 mm.; G, 650 mm.; H, 600 mm.; etc. The exact values, which can be determined with a cathetometer or by other suitable means, will of course always remain the same, and thus these predetermined pressures may always be duplicated at will. The lowest side tube, E, which is connected to a relay, is beneath the mercury surface at all times. The electrical circuit and precision of regulation of this modified regulator are similar to that described in Cox's article (*1*), where further details may be obtained.

[1] Received February 13, 1931.



A Modified Vacuum Regulator

Literature Cited

(1) Cox, Ind. Eng. Chem., Anal. Ed., **1**, 7 (1929).
(2) Weatherill, *J. Am. Chem. Soc.*, **47**, 1947 (1925).

Quantitative Estimation of Amaranth and Tartrazine in a Food Color Mixture[1]

O. L. Evenson and R. H. Nagel

Color Certification Laboratory, Food and Drug Administration, U. S. Department of Agriculture, Washington, D. C.

A quantitative estimation of certain food dyes, especially amaranth and tartrazine, which have practically the same solubility in organic solvents and therefore cannot be separated by the extraction method, may be made by employing selective reduction. In a mixture of amaranth and tartrazine, the amaranth is reduced by ammonium sulfide, leaving the tartrazine, which is then estimated by means of titanium trichloride. Another method, based upon spectrophotometric measurements, is also given.

IN THE analysis of food color mixtures it is generally possible to separate the various components from one another, prior to a quantitative estimation of each, by taking advantage of their different solubilities. In the case of amaranth (Colour Index 184) and tartrazine (Colour Index 640) this method has not been found feasible owing to the fact that their solubilities are very nearly the same in all of the many solvents that have been tried. Since amaranth and tartrazine are two of the most widely used food colors, it is quite important to be able to analyze quantitatively mixtures containing them. Jablonski (*6*) has recently developed an ingenious method for separating these two dyes, which, however, is very time-consuming.

In the first method recorded here, advantage is taken of the difference in stability of amaranth and tartrazine in the presence of a reducing agent. It was found that amaranth is quickly destroyed by ammonium sulfide, while tartrazine is relatively stable. When ammonium sulfide solution is added to a mixture of these two dyes, the amaranth is first reduced. The point at which the amaranth has been completely destroyed can be readily ascertained by careful observation, and the reaction stopped. The tartrazine is then determined in the usual manner, using standard titanium trichloride solution.

Materials

The ammonium sulfide solution was made by saturating concentrated ammonium hydroxide, specific gravity 0.9, with hydrogen sulfide. The titanium trichloride solution was made approximately 0.05 *N*, and standardized by two separate methods (*1*). The dyes were commercial, certified food colors from various manufacturers. In all titrations mentioned, the contents of the reaction flask were stirred vigorously by means of a mechanical stirrer, and kept under an atmosphere of carbon dioxide.

Experimental Procedure

Several mixtures containing known amounts of amaranth and tartrazine in varying proportions were made. From these mixtures aqueous solutions containing one gram of dye per 100 cc. of solution were prepared. Twenty-five cubic centimeters of this solution were placed in a 500-cc. wide-mouth Erlenmeyer flask, and a small quantity (1 to 10 cc.) of ammonium sulfide solution added. When the amaranth had been destroyed as evidenced by the color change from red to yellowish orange, the reaction was stopped by adding an excess, 10 to 30 grams, of sodium bitartrate, 75 cc. of water, and boiling the mixture. The sodium bitartrate, because of its acidic properties, reacts with the remaining ammonium sulfide, liberating hydrogen sulfide which is driven off by boiling. The sodium bitartrate also serves as a buffer in the titration of the tartrazine with standard titanium trichloride solution, which was the next step.

It was observed that variations in temperature noticeably affect the length of time necessary to reduce the amaranth. To illustrate this and to show the magnitude of the error introduced by not stopping the reaction between the ammonium sulfide and the dye till long after all the amaranth had been destroyed, experiments were performed as summarized in Table I. The temperature of the reaction was regulated by partially submerging the flask in a large vessel of water of the required temperature. In Table I, determinations A and B on mixture 3, and determinations B and D on mixture 1, show that a change of only 10° C. approximately doubled the time of reaction. Determinations A, B, and C on mixture 1 and B and C on mixture 3 show that the time elapsing before the reaction is stopped can vary considerably and concordant results may still be obtained. It has been found that it is not difficult to judge by the color changes when the reaction should be stopped and that there is quite an interval before appreciable amounts of tartrazine are destroyed. Determinations B, mixture 2, and D, mixture 3, illustrate the error introduced by allowing the reaction to continue for an unreasonably long time. If the reaction is stopped too soon, a distinct red color will appear when the sodium bitartrate and water are added, indicating the presence of undestroyed amaranth. Table I gives definite information as to temperature and time on mixtures of various composition, and may be used as a guide until the analyst obtains the little experience necessary to judge correctly the color changes involved.

Table I—Effect of Temperature and Amount of Amaranth upon Time of Reduction

Detn.	Mixture	Temp.	Amaranth Present	Tartrazine Present	Tartrazine Found	Time
		° C.	%	%	%	*Min.*
1	A	35	93.33	6.67	7.03	7½
	B	35	93.33	6.67	6.81	6½
	C	35	93.33	6.67	7.03	9
	D	25	93.33	6.67	6.91	14
2	A	32	56.3	43.7	44.1	6⅓
	B	32	56.3	43.7	42.4	12
3	A	35	25.0	75.0	74.25	4½
	B	25	25.0	75.0	74.25	9
	C	25	25.0	75.0	74.12	11
	D	25	25.0	75.0	72.76	20

After many trials the method described below was found to give the best results.

Selective Reduction Method

Using a dye mixture known to contain only amaranth and tartrazine, a 1 per cent aqueous solution was prepared. Twenty-five cubic centimeters of this solution were placed in a 500-cc. wide-mouth Erlenmeyer flask, and 2.5 cc. ammonium sulfide solution added. The contents of the flask were thoroughly mixed by imparting a gentle swirling motion,

[1] Received February 28, 1931. Presented before the Division of Dye Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

and the progress of the reaction which took place at room temperature was carefully observed over a white surface. When the amaranth had been destroyed as evidenced by the change of the red color of the solution to yellow or yellowish orange, the reaction was stopped by adding about 15 grams of sodium bitartrate, 75 cc. of water, and boiling the mixture. This yellow solution containing the tartrazine was then titrated, while hot, with the standard titanium trichloride solution. The percentage of tartrazine was then calculated, 0.01336 gram of tartrazine being equivalent to 1 cc. of 0.1 *N* titanium trichloride solution.

To determine the amount of amaranth present, another 25-cc. portion of the 1 per cent solution was diluted with 75 cc. of water, 15 grams of sodium citrate were added as a buffer, and the mixture titrated with standard trichloride. During this titration the dye mixture was kept at the boiling temperature, and towards the end point the standard solution was added very slowly to allow the tartrazine sufficient time to reduce. The end point in a tartrazine titration, using sodium citrate as a buffer, is not so clear as when sodium bitartrate is used, but is definite and should cause no difficulty. Sodium bitartrate was not used in this case, as it has been shown to give low results for amaranth (*2*), while sodium citrate gives equally correct results for both amaranth and tartrazine (*3*). The volume of standard solution consumed by the amaranth is equal to the difference between that required to reduce the tartrazine, which was previously determined, and the total for the mixture. The percentage of amaranth was then calculated, 0.01511 gram of amaranth being equivalent to 1 cc. of 0.1 *N* titanium trichloride.

Typical results obtained on mixtures of known composition by the method discussed above and the method to be discussed subsequently are shown in Table II. Duplicate determinations are given in several cases to show the agreement between them.

Table II—Typical Results Obtained by Selective Reduction and Spectrophotometric Methods

Mixture	Tartrazine			Amaranth				
	Present %	Found by selective reduction %	Error %	Present %	Found by selective reduction %	Error %	Found by spectrophotometer %	Error %
1	93.33	92.84	−0.49	6.67	6.27	−0.40	6.68	+0.01
		92.55	−0.78		6.58	−0.09	6.42	−0.25
2	83.33	82.75	−0.58	16.67	17.44	+0.77	17.0	+0.33
		82.50	−0.83		17.74	+1.07	17.1	+0.43
3	75.00	74.5	−0.50	25.00	24.6	−0.40	24.6	−0.40
		74.25	−0.75		24.75	−0.25		
4	50.00	49.90	−0.10	50.00	49.4	−0.60	50.0	0.00
5	30.00	29.6	−0.40	70.00	71.0	+1.00	70.6	+0.40
6	6.67	6.9	+0.23	93.33	91.8	−1.53	91.7	−1.63
							96.0	+2.67
7	37.5	37.3	−0.2	62.50	62.0	−0.50	64.2	+2.30
							63.7	+1.20
8	4.74	5.1	+0.36	95.2	94.7	−0.50		
9	15.84	15.98	+0.14	84.16	82.75	−1.41		
10	20.00	19.6	−0.40	80.0	79.3	−0.70		
11[a]	1.00	1.3	+0.30	99.0	99.2	+0.20		

[a] On account of small quantity of tartrazine present, a 1-gram sample of mixture was taken for analysis, using correspondingly larger amounts of reagents.

It was found that a mixture of orange I and tartrazine could also be analyzed by the selective reduction method given above. In fact, it should be possible to separate any two dyes that show marked differences in stability by selecting a reducing agent that would destroy one and not attack the other.

Spectrophotometric Method

Another method of determining quantitatively the per cent of each component in a dye mixture is based upon the principle, known as Beer's law, that in a spectrophotometric measurement the extinction coefficient varies directly with the dye concentration, provided a solvent is used in which the dye does not show alteration with changes in concentration. Holmes (*4*) has found that an alcoholic solution meets this requirement. The procedure given here is a specific application of a general method which has been discussed by various investigators (*5*, *7*, *8*).

The first step was to establish two reference curves representing 100 per cent amaranth and 100 per cent tartrazine, respectively. Measurements of the extinction coefficients were made at various wave lengths throughout the visible spectrum on samples of amaranth and tartrazine from several manufacturers. A Bausch & Lomb spectrophotometer was used. These extinction coefficients were plotted against the corresponding wave lengths, resulting in curves similar to those shown in Figure 1.

Great care was taken to make the amaranth curve as accurate as possible, as it established a reference point which was used in all of the other determinations. Four samples of amaranth, each from a different manufacturer, were used. First the per cent of pure coal-tar dye in each sample was carefully determined by titration with standard titanium trichloride solution. Using these values, aqueous solutions

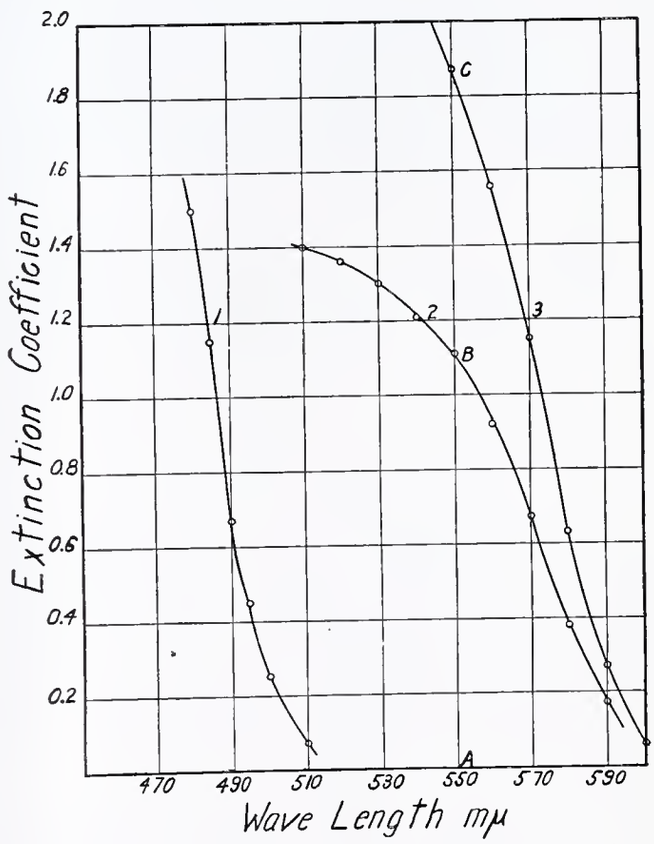


Figure 1—Reference Curves Used in Spectrophotometric Method

Curve 1—Tartrazine only, 20 mg. per liter (100%)
Curve 2—Amaranth, 12 mg. per liter (60%); tartrazine, 8 mg. per liter (40%)
Curve 3—Amaranth only, 20 mg. per liter (100%)

containing 1 gram of pure dye in 100 cc. of solution were made up. For the spectrophotometric measurements these solutions were diluted with water and alcohol until a concentration of 20 mg. of dye per liter of 50 per cent alcohol was obtained. A 3-cm. layer of this liquid was used in the spectrophotometer. The curves representing these four samples of amaranth proved to be remarkably close together. Curve 3, Figure 1, is an average curve for amaranth.

To estimate the per cent of amaranth in an amaranth-tartrazine mixture, a solution was made up containing 20 mg. of dye per liter of 50 per cent alcohol. The extinction co-

efficient was measured at a wave length of 550 millimicrons using a 3-cm. layer of solution. At this wave length it was found that the extinction coefficient of tartrazine is negligible. This value was then divided by 1.87, the extinction coefficient of pure amaranth at this wave length, and multiplied by 100. This gave the per cent amaranth present. When there was only a small per cent of amaranth present, it was found advantageous to use a dye concentration greater than 20 mg. per liter and reduce the reading by direct proportion to a basis of 20 mg. per liter. Curve 2, Figure 1, which represents measurements on a dye mixture composed of 60 per cent amaranth and 40 per cent tartrazine, illustrates the basis of the calculation just given. Between wave lengths 550 and 590, the altitude of any point on curve 2 is very nearly 60 per cent of the altitude of a corresponding point on the amaranth curve. For example, in Figure 1, at a wave length of 550, the distance AB = 59.4 per cent of AC. Results obtained by this method are shown in Table II.

Knowing the per cent of amaranth present, the per cent of tartrazine can be calculated from the volume of standard titanium trichloride solution necessary to titrate a given weight of the dye mixture. For example, 0.25 gram of the above dye mixture required 34.84 cc. of 0.05 N titanium trichloride solution. On the same basis, one gram of the dye mixture would require 69.68 cc. of 0.1 N titanium trichloride solution. As determined above by the spectrophotometer, there is 59.4 per cent of amaranth present, or 0.594 gram in one gram of dye mixture. This quantity of amaranth would require 0.594/0.01511, or 39.31 cc. of 0.1 N titanium trichloride solution. The difference between 69.68 cc. and 39.31 cc., or 30.37 cc., represents the quantity of reducing solution required for the tartrazine. The percentage of tartrazine then equals 30.37 × 0.01336 × 100, or 40.47. This calculation is analogous to that performed in estimating the amaranth by the selective reduction method given in this paper and may be summarized in the following equation:

$$A - \frac{b}{0.01511} \times 0.01336 \times 100 = \%\ \text{tartrazine}$$

When

A = cc. of 0.1 N titanium trichloride required by 1 gram of dye mixture

b = gram amaranth present in 1 gram of dye mixture

Conclusion

Of the two methods presented in this paper the selective reduction method is perhaps the better. It has the advantage of being more uniformly accurate and it does not take any special equipment. Both methods have the advantage of being rapid, requiring only a few minutes for each determination, and, as shown by the tables included, give fairly consistent and reasonably satisfactory results.

Literature Cited

(1) Ambler, J. A., Clarke, W. F., Evenson, O. L., and Wales, H., U. S. Dept. Agr., *Bull.* **1390**, 26 (1927).
(2) Evenson, O. L., and McCutchen, D. T., Ind. Eng. Chem., **20**, 860 (1928).
(3) Evenson, O. L., and Nagel, R. H., *Ibid.*, Anal. Ed., **3**, 167 (1931).
(4) Holmes, W. C., *Am. Dyestuff Reptr.*, April, 247 (1926).
(5) Holmes, W. C., *Ibid.*, March 22, 189 (1926).
(6) Jablonski, C. F., *J. Assocn. Official Agr. Chem.*, **12**, 354 (1929); **13**, 412 (1930).
(7) Mathewson, W. E., "Allen's Commercial Organic Analysis," p. 500, 5th ed., Vol. 5, Blakiston.
(8) Wales, H., *Am. Dyestuff Reptr.*, **12**, 751, 791, 855, and 863 (1923).

Analysis of Three Hydrocarbons by Combustion[1]

Kenneth A. Kobe

School of Chemistry, University of Minnesota, Minneapolis, Minn.

COMBUSTION data in gas analysis are generally used to determine hydrogen and a hydrocarbon, or two hydrocarbons, and it is not generally recognized that it is possible to determine three hydrocarbons in one combustion. DeVoldere and deSmet (*2*, *3*) have divided gases into three classes, and deduced relationships between these classes, and series within the classes, which show when it is possible to determine three hydrocarbons by a single combustion. Much simpler relations can be deduced from the general formulas of any three hydrocarbons by the use of determinants, avoiding the necessity of fixing the class and series of which the gas is a member.

It is not necessary that the gas be a hydrocarbon, since values for other gases can be inserted into the formula with the same result. Table I gives the equivalent values for other gases.

Table I—Equivalent Values for Other Gases

Gas, C_aH_b	a	b
Hydrogen, H_2	0	2
Carbon monoxide, CO	1	−2
Carbon dioxide, CO_2	1	−4
Oxygen, O_2	0	−4
Formaldehyde, CH_2O	1	0
Dimethyl ether, $(CH_3)_2O$	2	4

Thus the term "hydrocarbon" as used here will also include these gases.

Determination of Three Hydrocarbons

If nitrogen is not present in the mixture or is determined by actual difference, the calculations can be made from the volume of gas used, the volume of carbon dioxide formed, and the contraction in volume occurring on combustion.

V = volume of gas used
C = volume of carbon dioxide formed
U = contraction in volume on combustion
x = cc. of hydrocarbon C_aH_b
y = cc. of hydrocarbon C_cH_d
z = cc. of hydrocarbon C_eH_f

The general equation for the combustion of a hydrocarbon is

$$C_aH_b + (a + b/4)\ O_2 \longrightarrow a\ CO_2 + b/2\ H_2O$$

This leads to the equations

$$V = x + y + z \quad (1)$$
$$C = ax + cy + ez \quad (2)$$
$$U = (1 + b/4)x + (1 + d/4)y + (1 + f/4)z \quad (3)$$

The determinant D of this set of equations is

$$D = \begin{vmatrix} 1 & 1 & 1 \\ a & c & e \\ 1 + b/4 & 1 + d/4 & 1 + f/4 \end{vmatrix}$$

$$D = \frac{ad + be + cf - af - bc - de}{4} \quad (4)$$

The Equations 1, 2, and 3 are dependent if $D = 0$, in which case

$$ad + be + cf = af + bc + de \quad (5)$$

Thus if Equation 5 is an equality, it will not be possible

[1] Received February 13, 1931.

to determine the three hydrocarbons, and conversely, if the two sides of the equation are not equal, then it is possible to calculate the three hydrocarbons from Equations 1, 2, and 3.

In the case of a homologous series

$$b = am + n, d = cm + n, \text{and} f = em + n$$

substituting these values in Equation 5 we find that the equality holds, that $D = 0$, so it is not possible to solve these equations for three hydrocarbons of the same homologous series. However, if the third hydrocarbon is of another series, the identity of Equation 5 does not hold, so it is possible to determine the three hydrocarbons. If all three hydrocarbons are of different series, the values of the subscripts must be inserted in the equation to find if the identity is true.

Solving Equations 1, 2, and 3, the general values for x, y, and z are:

$$x = \frac{V\left(c - e + \frac{cf - de}{4}\right) + C\left(\frac{d - f}{4}\right) + U(e - c)}{D}$$

$$y = \frac{V\left(e - a + \frac{be - af}{4} + C\left(\frac{f - b}{4}\right) + U(a - e)\right.}{D}$$

$$z = \frac{V\left(a - c + \frac{ad - bc}{4}\right) + C\left(\frac{b - d}{4}\right) + U(c - a)}{D}$$

$$D = \frac{ad + be + cf - af - bc - de}{4}$$

Determination of Three Hydrocarbons and Nitrogen

Nitrogen is usually determined by difference from the sum of all gases present. However, it may be determined from the combustion data. Its presence in the hydrocarbon mixture adds one more gas so that a fourth equation is necessary for the determination of the composition. This will be given by the volume of oxygen consumed in the combustion of the hydrocarbons.

W = volume of oxygen used in the combustion

$$W = (a + b/4)x + (c + d/4)y + (e + f/4)z \qquad (6)$$

Equations 2, 3, and 6 now can be solved for x, y, and z, the volume of nitrogen being the difference between the volume taken and the sum of these gases. The determinant of these equations is

$$D = \begin{vmatrix} a & c & e \\ 1 + b/4 & 1 + d/4 & 1 + f/4 \\ a + b/4 & c + d/4 & e + f/4 \end{vmatrix}$$

$$D = \frac{af + bc + de - ad - be - cf}{4} \qquad (7)$$

This reduces to Equation 5

$$ad + be + cf = af + bc + de \qquad (5)$$

Thus the same relationship tells whether or not the equations are dependent so that three hydrocarbons can be determined in the presence of nitrogen by the use of the volume of oxygen consumed in the combustion.

The general values for x, y, and z are:

$$x = \frac{C\left(e - c + \frac{f - d + de - cf}{4}\right) + U\left(\frac{de - cf}{4}\right) + W\left(c - e + \frac{cf - de}{4}\right)}{D}$$

$$y = \frac{C\left(a - e + \frac{b - f + af - be}{4}\right) + U\left(\frac{af - be}{4}\right) + W\left(e - a + \frac{be - af}{4}\right)}{D}$$

$$z = \frac{C\left(c - a + \frac{d - b + bc - ad}{4}\right) + U\left(\frac{bc - ad}{4}\right) + W\left(a - c + \frac{ad - bc}{4}\right)}{D}$$

$$D = \frac{af + bc + de - ad - be - cf}{4}$$

Although there are four equations (1, 2, 3, and 6) it is not possible to determine four hydrocarbons since the equations are dependent, being related by the equation

$$U = V + W - C \qquad (8)$$

Application of Method

The determination of carbon monoxide, hydrogen, and methane by this method has been known for some time (*7*). The new apparatus devised by Shepherd (*6*) makes use of this method for the determination of these three gases. The method of manipulation for the determination of any three gases is the same as that used for carbon monoxide, hydrogen, and methane, and may be carried out by the instructions given for either style of apparatus (*6*, *7*). It is seen that the general equations reduce to very simple ones when specific values are substituted for the general terms, so that the calculations involved are no more difficult than those of an ordinary combustion. Not only can a gas of another series be determined in the presence of two saturated hydrocarbons, but two unsaturated hydrocarbons may be determined in the presence of a third gas, an advantage since both unsaturates would be absorbed in the usual method. The method lends itself to the analysis of the products from catalytic and pyrolytic reactions, and many other uses for specific problems can be worked out.

Errrors of Method

The correctness of these results, as those of all methods in gas analysis, assumes that volumes of gases are additive and that the volume of carbon dioxide formed in a combustion is an exact multiple of the volume of hydrocarbon consumed. Fuchs (*4*) has shown that there is an increase in volume on mixing carbon dioxide with nitrogen or with oxygen. With the former gas the maximum increase was 2.73 per cent at 56.7 per cent nitrogen, while with the latter gas the maximum increase was 2.45 per cent at 53.0 per cent oxygen. Also, carbon dioxide does not have as great a molecular volume as methane or carbon monoxide, so that the combustion of these gases does not produce an equal volume of carbon dioxide but a slightly smaller volume (*1*). Corrections for these effects are not ordinarily applied, but in certain cases they cause appreciable error and correction should be made.

In the use of this method it may be emphasized that combustion by the slow-combustion method (*5*) gives rise to less error than the explosion method since the sample and oxygen used are larger. The use of this method involves but one more measurement than the ordinary combustion for, after the carbon dioxide has been absorbed, the excess oxygen left from the combustion is absorbed. It is apparent that this one measurement cannot appreciably increase the error of the determination. The error calculated by Shepherd for his combustion does not give differences greater

than one-tenth of one per cent for the technical method, and would be less for the exact method.

Literature Cited

(1) Dennis and Nichols, "Gas Analysis," p. 134, MacMillan, 1929.
(2) Dennis and Nichols, *Ibid.*, p. 123.
(3) deVoldere and deSmet, *Z. anal. Chem.*, **49**, 661 (1910).
(4) Fuchs, *Z. physik. Chem.*, **92**, 641 (1918).
(5) Kobe, Ind. Eng. Chem., Anal. Ed., **3**, 159 (1931).
(6) Shepherd, *Bur. Standards J. Research*, **6**, 121–67 (1931).
(7) U. S. Steel Corporation Chemists, "Methods for Sampling and Analysis of Gases," pp. 62 and 98, Carnegie Steel Co., Pittsburgh, 1927.

Determination of Organic Acids

V—Application of Partition Method to Quantitative Determination of Acetic, Propionic, and Butyric Acids in Mixture[1,2]

O. L. Osburn and C. H. Werkman

Department of Bacteriology, Iowa State College, Ames, Iowa

The partition method has been extended to the quantitative determination of acetic, propionic, and butyric acids in a mixture. A nomogram has been constructed from which is read the percentage of each of the three acids present after two values (percentage partition constants) characteristic of the mixture have been determined.

The differential distribution of fatty acids between two immiscible solvents has been employed in a partition method for (*a*) the quantitative determination of two known fatty acids in a mixture (*2*, *3*), and (*b*) the provisional identification of two fatty acids in a mixture (*5*). The method was developed to fill a need in fermentation studies for rapid and accurate determinations of the lower fatty acids. For a consideration of the principles and advantages of the partition method, the reader is referred to Behrens (*1*) and to previous publications in this series (*2*, *3*, *4*, *5*).

The partition method is extended in the present paper to the quantitative determination of acetic, propionic, and butyric acids in a mixture. The method has yielded excellent results in this laboratory and with reasonable care will give results with an error of less than 5 per cent for each acid. Its most severe test is in the case of a mixture containing a small proportion of one or two of the acids.

In conducting the quantitative determination according to the partition method, the unknown acid solution is partitioned with isopropyl ether. If the isopropyl ether is of a commercial grade it should be purified by adding an excess of a solution of 5 per cent sodium hydroxide. After the mixture is shaken, the ether is decanted and dried by adding calcium chloride. It is then distilled and the portion coming over at constant temperature is collected for use. The commercial product develops an acidity upon standing.

In determining the quantitative relationships of two acids in a mixture, only one partition value characteristic of the mixture is necessary, whereas two values are necessary in the determination of three acids. Such partition values may be obtained in a number of ways: (1) The unknown acids may be serially partitioned, a method suggested by Behrens (*1*). In this method one of the phases is again partitioned and a second value obtained. Serial partition has not been found satisfactory. Its use did not yield results of the degree of accuracy or sensitivity desired. (2) Successive partition of the acids between water and a suitable immiscible solvent, and water and a second immiscible solvent. This method has been employed in the provisional identification of two acids in a mixture (*5*). (3) Two separate partitions of the aqueous solution of acids using one immiscible solvent but in different proportions. This type of partition has yielded the most satisfactory results and has been chosen for the determination of three acids.

In former publications (*2*, *3*, *4*, *5*) the partition value characteristic of the mixture of acids has been called the partition constant (P') and was defined as the number representing the cubic centimeters of 0.1 N alkali required to neutralize 25 cc. of the aqueous phase to phenolphthalein, when 30 cc. of the unknown 0.1 N acid solution were partitioned with 20 cc. of the immiscible solvent. It is necessary in using partition constants to adjust the unknown acid solution to 0.1 N. If, instead of adjusting the acid solution to exactly 0.1 N and determining the partition constant, the quantity of acid distributed in the aqueous phase be calculated as the per cent of the total acid in an equal volume of the unknown solution, it becomes unnecessary to adjust the acid solution to exactly 0.1 N. It has been found necessary to adjust only to within the limits of 0.12 N and 0.08 N. Of course, the final adjustment must be known accurately. This percentage is termed the percentage partition constant (K) to differentiate it from the partition constant (P').

The two values of K employed to determine the percentages of each of the three acids in solution are:

K_1 equals percentage of acid in the aqueous phase when 30 cc. of the unknown acid solution, adjusted to a normality between 0.12 and 0.08, are partitioned with 60 cc. of isopropyl ether at 25° C. K_2 is determined by using 30 cc. of the acid solution and 15 cc. of isopropyl ether. M represents the number of cubic centimeters of 0.1 N alkali required to neutralize 25 cc. of the unknown solution. M_2 represents the number of cubic centimeters of 0.1 N alkali required to neutralize 25 cc. of the aqueous phase after partition.

The solvents are shaken in a separatory funnel for 1 minute, and 3 minutes are then allowed for the phases to separate when 25 cc. of the aqueous layer are withdrawn for titration.

$$K_1 = \frac{M_2}{M} \times 100 \qquad (1)$$

The percentage partition constants (K, 30 cc. acid, and 60 cc. ether) established for the three acids are:

Acetic acid	$K_1 = 91.5$
Propionic acid	$K_1 = 70.5$
Butyric acid	$K_1 = 39.8$

In like manner, by extracting 30 cc. of each acid with 15 cc. of isopropyl ether at 25° C., there is established a second set of percentage partition constants:

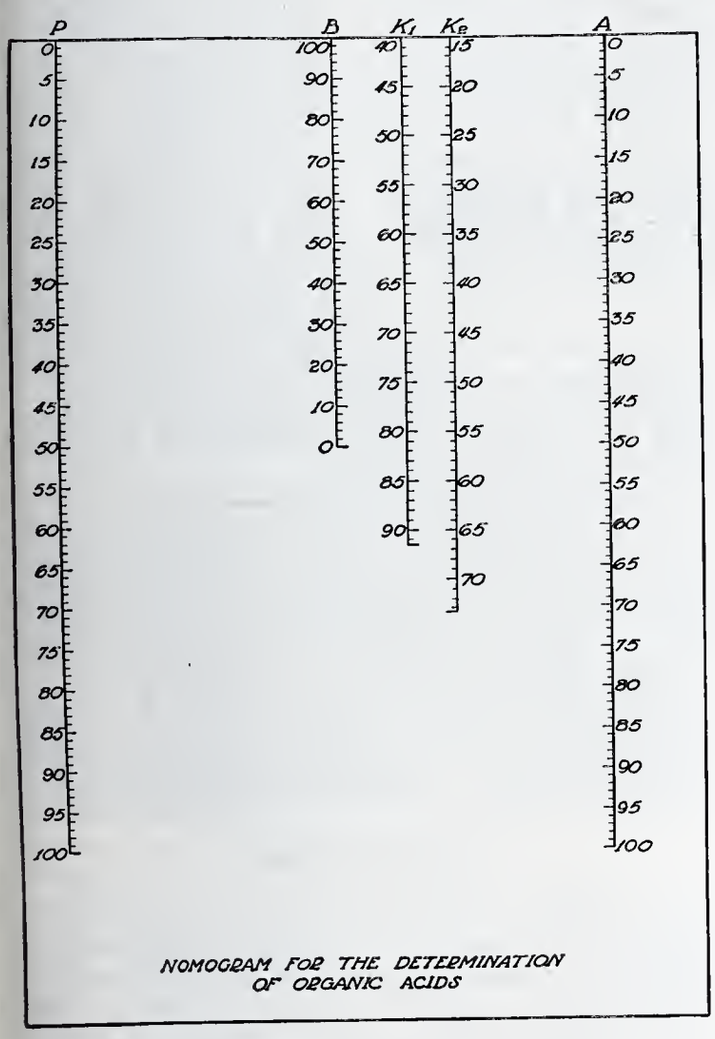
[1] Received February 26, 1931.
[2] Supported by an appropriation from Industrial Research funds of Iowa State College, as a part of the program for the study of the use of wastes by fermentation.

Acetic acid	$K_2 = 73.5$
Propionic acid	$K_2 = 38.8$
Butyric acid	$K_2 = 15.0$

Throughout the following discussion, A will designate per cent of acetic; P, per cent of propionic; and B, per cent of butyric acid in the acid solution.

Whatever the composition of the unknown solution of acids may be, it is evident from the two sets of constants established that

$$K_1 = 0.915\,A + 0.705\,P + 0.395\,B, \text{ and}$$
$$K_2 = 0.735\,A + 0.388\,P + 0.15\,B$$



Consequently, for each possible value of K_1, there must be for each mixture a corresponding value of K_2. K_2 is calculated as given above. For example, if $K_1 = 60$, then when $A = 0$,

$$K_2 = 0.735 \times 0 + 0.388 \times 66.5 + 0.150 \times 33.5 = 30.6$$

and when for the same value of K_1, $A = 40.2$,

$$K_2 = 0.735 = 40.2 + 0.388 \times 0 + 0.15 \times 59.8 = 38.4$$

It is evident that for each value of K there is a minimum and maximum value of K_2, and furthermore, for each intermediate ternary mixture, there can be one and only one value of K_2, and this value must lie between the two limiting values of K_2.

It is also true that if K_2 lies at any fractional distance between its limiting values, then A, P, and B must also be at the same fractional distance between their limits. For example, if $K = 60$, and the experimental value of $K_2 = 34.5$—i. e., half way between the limits of K_2—then A, P, and B are fixed at values half way between their limits and

$$A = \frac{40.2 - 0}{2} = 20.1,\ P = \frac{66.5 - 0}{2} = 33.25, \text{ and}$$
$$B = 33.5 + \frac{(59.8 - 33.5)}{2} = 46.7$$

With the foregoing facts at hand, it is possible to construct a nomogram such as that shown in the accompanying figure. The accuracy of the nomogram can be checked. If any value of K_1 is selected and straight lines are drawn through it and through the limiting values of K_2, then the lines should intercept the same limits of A, P, and B as those given by solution of the simultaneous equations.

Analytical Procedure

About 100 cc. of the acid mixture should be at hand. Titrate 25 cc. and adjust accurately to any normality between 0.12 and 0.08. Then partition two 30-cc. portions, one portion with 60 cc., the other with 15 cc. of the isopropyl ether at 25° C. as described. Withdraw 25-cc. portions of the water layers, titrate, and calculate the values K_1 and K_2. A straight edge laid across these two points on the nomogram intersects A, P, and B and indicates the per cent of each acid present. About 10 minutes are required for the complete procedure. Representative analyses determined by use of the nomogram are shown in Table I.

Table I—Representative Analyses

Analysis	Acid	Amount Present	Amount Found
		%	%
I	A	90	89.0
	P	5	7.5
	B	5	4.0
II	A	40	40.5
	P	30	28.5
	B	30	30.5
III	A	30	29.5
	P	10	10.5
	B	60	60.5
IV	A	70	70.2
	P	5	3.0
	B	25	25.5

A, P, and B may also be evaluated by solving the three simultaneous equations by which the nomogram was constructed:

$$\begin{aligned} 0.915\,A + 0.705\,P + 0.398\,B &= K_1 \\ 0.735\,A + 0.388\,P + 0.15\,B &= K_2 \\ A + P + B &= 100 \end{aligned}$$

The values of K_1 and K_2 for the pure acids vary with the relative concentration of the acids and with the temperature, and serious errors will result if the total normality of the acid mixture to be analyzed is not near 0.1 N (0.08 to 0.12 N). The temperature should be between 24° and 26° C.

This method can be adapted to mixtures of these three acids at any normality from 0.2 to 0.02 by establishing the variation of K_1 and K_2 with the concentration of the acids. These values can then be plotted on a graph as abscissas against volumes of ether as ordinates. In this manner it is quite simple to read off the volumes of ether to use with 30 cc. of the acids to obtain constants equal to those obtained.

It is to be expected that in a solution containing a small per cent of butyric or propionic acid, the values of K_1 and K_2 will be slightly higher than the true values. This has been noticed to a certain extent. Somewhat larger errors are apparent in Table I when P and B are in the neighborhood of 5 to 10 per cent.

Literature Cited

(1) Behrens, *Z. anal. Chem.*, **69**, 97 (1926).
(2) Werkman, Ind. Eng. Chem., Anal. Ed., **2**, 302 (1930).
(3) Werkman, *Iowa State College J. Sci.*, **4**, 459 (1930).
(4) Werkman, *Ibid.*, **5**, 1 (1930).
(5) Werkman, *Ibid.*, **6**, 121 (1931).

A Dry Method of Microanalysis of Gases[1]

Francis E. Blacet and Philip A. Leighton

DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, CALIF.

An apparatus for microanalysis of gases has been described and a method worked out for the analysis of gas samples of the order of 25 to 100 cu. mm. without the use of liquid reagents.

Yellow phosphorus has been used to remove oxygen, fused potassium hydroxide to remove carbon dioxide, and fused phosphorus pentoxide to remove water vapor. These absorbents were used also in the analysis by combustion of hydrogen, carbon monoxide, and methane.

The results of the analysis of a number of different samples are given. These indicate that the degree of precision to be expected by this method is of the same order of magnitude as that ordinarily attained in macroanalysis of gases.

THE increasing importance in photochemical work of analyzing gas samples of the order of 0.1 cc. or less has caused the authors to spend some time in the study of micro methods. It was desired to avoid the elaborate methods of Langmuir (*4*) and Ryder (*6*). The apparatus of Guye and Germann (*3*) has the serious disadvantage of containing many stopcocks in which appreciable loss of gas may occur. Reeve (*5*) has proposed a much simpler apparatus for the determination of carbon dioxide by means of fused potassium hydroxide. Christiansen (*1*) employed a similar device but used the liquid reagents of macroanalysis.

The method of liquid reagents has the advantage of wider applicability at the present time because in macroanalysis they have been used almost exclusively and much of this accumulated knowledge can be used in micro methods. However, the solubility of the sample in the various reagents and washing solutions may cause an error of serious magnitude when very small quantities of gases are involved. This is because the total volume of the various solutions with which the gas must come in contact is proportionately much greater than in macroanalysis. Also, in using a capillary buret it has been found very difficult if not impossible to free the walls entirely of a film of water solution by replacement with mercury. This film must be dealt with in volume measurements and unless great care is exercised, upon the introduction of another solution, it may be the cause of a precipitate forming in the buret, which may be very hard to remove. Theoretically, at least, the use of solids as absorbents in conjunction with the microburet would eliminate these objections. The authors have investigated this method and have been able to analyze with some degree of precision samples of the general order of magnitude of 25 to 100 cu. mm. for water vapor, carbon dioxide, oxygen, carbon monoxide, hydrogen, and methane entirely without the use of water solutions.

Apparatus

Figure 1 is a diagram drawn to scale of the apparatus employed. *A* is a water-jacketed microburet. This is a capillary tube of approximately 0.5 mm. in diameter and accurately ruled in millimeter divisions for a length of 45 cm. It was calibrated by means of weighing drops of mercury and was found to have a volume of approximately 1 cubic millimeter for 4 linear millimeters. Thus the total capacity is about 112 cu. mm. The upper end is bent as shown and ends in a capillary of small external diameter to facilitate the intake and discharge of gases. The tip of this capillary is ground and fire-polished to a radius of curvature somewhat less than that of the top of the gas holders *H* and *J*. The lower end of the buret is sealed to a larger tube containing a trap to insure the exclusion from the capillary of impurities and chance solid material which may be introduced in the sealing process. To the bell-shaped lower end is attached a short length of very heavy rubber pressure tubing. In setting up the buret, it is first inverted and filled completely with mercury and a plug sealed in the free end of the pressure tubing. When in position for use, the rubber tubing fits in the jaws of an especially heavy buret clamp equipped with a finely threaded screw, *B*. By means of this screw the mercury level in the buret can be changed with precision. This device was preferred to the steel screw and hard rubber manipulator proposed by Christiansen (*1*), for, owing to the pressure developed in a buret of this length, it was found impossible to prevent the escape of mercury past the screw.

By means of the telescoped brass tubes *C* and *D* and the machined screw *E*, everything on the table, *F*, can be moved up or down with perfect control. *G* is a mercury reservoir of 7 cm. diameter. *H* and *J* are the containers for the gas samples and are also used for the processes of absorption and explosion, as will be explained later. They have a capacity of approximately 2 cc. each. In the diagram only two of these are shown, but, in fact, four of them are symmetrically attached by means of circular steel springs to the revolving table *M*. *K* is a brass tube which acts as a guide for accurately placing and supporting an absorbent holder, *L*.

Methods of Procedure

For simplicity in explaining the method of using this apparatus, let it be supposed that it is desired to determine the percentage of oxygen in dry air. First the containers *H* and *J* are filled with mercury. This is done by placing a glass tube, which has been drawn out to a capillary and properly bent, so that its end will go down into the reservoir *G* and up to the top on the inside of the containers. If the containers are clean and have a top of smooth curvature all the air can be drawn out with ease. The high surface tension of mercury facilitates this. Several hundred cubic millimeters of the air are introduced into *H*. This constitutes the sample for analysis upon which several determinations presumably are to be made. If a Toepler pump is used for the purpose of introducing samples, its outlet is bent in the same manner as the tip of the buret and placed permanently in position in the reservoir and at the same height as the buret tip. The rotating table *M* is mounted on an adjustable arm so that the containers can not only rotate completely around the central shaft but may be moved to any desired position within the reservoir. Accordingly, the outlet for the Toepler pump may be at the back side of the reservoir and a container can be moved over its tip and filled.

The next step is to obtain a known volume for analysis. By means of the screw *B* all of the air in the buret is replaced by mercury. The tip must be under the surface of the mercury in *G* while this is done, otherwise when it is submerged it will

[1] Received March 7, 1931.

invariably carry a small air bubble with it. *H* is now placed directly over the tip, and by lowering the table *F*, the tip is brought into the gas sample. By means of *B* a portion of the sample is drawn into the buret. The volume ordinarily taken varies from 25 to 100 cu. mm. depending upon the total amount available and the subsequent treatment to which it is to be subjected. The table is then raised so that the level of the mercury in the reservoir is on the level with the uppermost calibration mark in the water-jacketed part of the buret. By further unscrewing *B*, the gas, followed by a thread of mercury, is brought into the calibrated portion for measurement of its volume. When its upper level is at the same height as the surface of the mercury in the reservoir, it is then theoretically under atmospheric pressure. However, the apparent pressure in the buret may be considerably in error, owing to the fact that mercury has a tendency to stick to clean dry glass. If no precautions are taken two subsequent volumes on the same gas sample may be obtained which vary as much as 1 per cent from one another. To reduce this source of error two expedients are used. First, the buret is gently tapped with the finger as the gas is being brought to the desired position. Second, five independent readings are always recorded and the average taken in calculating the volume. These precautions reduce the probable error in all cases below 0.2 per cent.

After the volume readings for the run have been recorded along with temperature and barometric readings, container *J* is brought over the buret tip and the gas in the buret expelled into it. The gas is now ready to have the oxygen absorber introduced. The removable holder *L* has a platinum loop sealed in its tip. In this loop is fused a small bead of yellow phosphorus. The fusion may ordinarily be done by placing a fresh piece of phosphorus in the loop by means of forceps and then holding it over a warm resistance coil or even in the sunlight. By quickly removing when fusion occurs and placing it under the mercury, spontaneous combustion may be avoided. In any case it should not be allowed to remain in the air any length of time, for the moisture of the air along with oxygen causes a film of phosphoric acid to coat the bead, thus making it a much slower absorber. As shown in Figure 1, the holder is placed in the guide *K*. The container *J* is brought into position and the phosphorus introduced into it. In this operation care must be taken not to allow the glass of the holder *L* to touch the walls of the container. It has been found that a cold tube introduced into mercury in this way is coated with a film of air, part of which will be imparted to the walls of *J* if contact is made between the two glass surfaces. On this account the guide is necessary for the introduction of the absorber up the center of the container. The height of *K* is also arranged so that only the phosphorus bead and a little platinum wire enters the gas bubble.

Fifteen minutes has been found sufficient time to allow for complete absorption in practically all cases. However, absorption to constant volume is practiced. After absorption has occurred and the absorbent removed, the tip of the buret is brought to the top of the container (more accurately, the top of the container is brought to the buret tip) and the residual gas taken into the buret. With the proper manipulation of *B*, *E*, and *M*, this operation presents no practical difficulties. If the entire gas bubble is not drawn into the buret intact the first time, it need only be driven back into the container and the process repeated. The experimenter soon acquires skill in this regard. The volume of the residual gas is now measured and the temperature and the barometric pressure again recorded. The absorption process is repeated for 5 minutes more, and if no further reduction in volume occurs, all data necessary for the simple standard method of calculation of the determination are complete.

For the removal of moisture, a bead of fused phosphorus pentoxide is used. This may be prepared over a glowing electric coil. A flame should not be used because of the moisture generated by it.

Carbon dioxide is removed by means of fused potassium hydroxide. This reagent is prepared in the same way as the phosphorus pentoxide, except that after the bead is formed it must be allowed to collect moisture from the air until it presents a shining surface before placing under the mercury of the reservoir. This moisture is essential for the rapid absorption of the carbon dioxide. When potassium hydroxide was introduced while still very hot, it was found that as much as 2 hours was required before all the carbon dioxide was taken up.

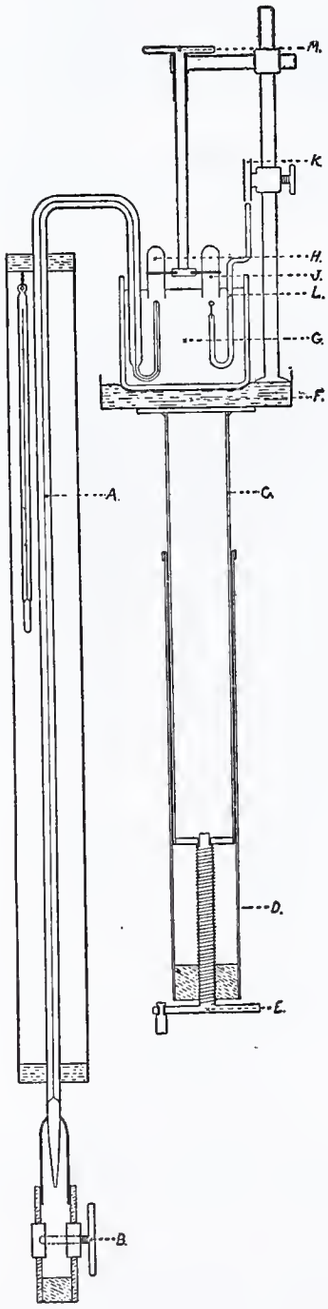


Figure 1—Diagram of Microburet and Manipulator

The use of these solid reagents in the quantitative determination of water vapor, oxygen, and carbon dioxide opens up the possibility of their use also in the analysis of the combustible gases hydrogen, carbon monoxide, and the simple hydrocarbons. Some combustions have been made in this laboratory with fair success. The apparatus used, in addition to that which has been described above, consists of the

Table I—Results of Analysis

Gases Analyzed	Determinations 1	2	3	4	Mean	Av. Deviation from Mean	Theoretical	Theoretical Minus Mean
					%	%	%	%
Oxygen in air:								
Vol. sample, cu. mm.	75.40	95.39	102.60	100.61				
Percentage O_2	20.8	20.7	20.6	20.8	20.75	0.08	20.9 (2)	−0 15
Carbon dioxide from oxalic acid:								
Vol. sample, cu. mm.	88.16	79.81	79.16	100.90				
Percentage CO_2	49.5	49.7	49.4	49.5	49.52	0.08	50.0	−0.5
Carbon dioxide in unknown:								
Vol. sample, cu. mm.	75.89	84.92	75.42	87.68				
Percentage CO_2	27.0	26.9	26.9	27.0	26.95	0.05		
Electrolytic hydrogen:								
Vol. sample, cu. mm.	63.66	66.45	68.39	67.76				
Vol. oxygen for combustion, cu. mm.	96.00	97.25	106.80	110.40				
Percentage H_2	100.2	100.1	100.4	100.4	100.3	0.1	100.0	+0.3
Methane from calcium acetate and soda lime:								
Vol. sample, cu. mm.	26.11	30.48	26.05	30.17				
Vol. oxygen for combustion, cu. mm.	100.+	100.+	100.+	100.+				
Percentage CH_4	97.2	97.1	96.7	98.5	97.4	0.6	100.0 (?)	−2.6
Mixture of hydrogen and methane:								
Vol. sample, cu. mm.	58.40	55.53	55.95	58.78				
Vol. oxygen for combustion, cu. mm.	106.55	108.10	106.97	108.06				
Percentage H_2	51.9	49.0	51.5	48.2	50.1	1.6	50.4	−0.3
Percentage CH_4	48.7	51.6	49.3	48.1	49.7	1.0	48.3 (?)	−1.4
Mixture of hydrogen and carbon monoxide:								
Vol. sample, cu. mm.	58.57	58.35	61.12					
Vol. oxygen for combustion, cu. mm.	93.56	106.11	104.72					
Percentage H_2	49.0	54.0	52.9		51.3	2.2	50.4	+0.9
Percentage CO	48.3	49.2	49.5		49.0	0.5	49.6	−0.6

ordinary Ruhmkorff coil of gas analysis and special electrodes constructed in the following manner:

A piece of glass tubing having an external diameter of 2 mm. and about 13 cm. in length is placed within a 4-mm. tube of 12 cm. in length so that at one end the tubes are flush with one another. Then two platinum wires about 14 cm. long are placed one inside the 2-mm. tube and the other in the space between the inner and outer tube in such a way that both extend about 1 mm. beyond the flush ends of the tubes. These ends are then carefully fused, closing the tubes and leaving two insulated electrodes about 1 mm. apart. These electrodes are broken off at the surface leaving an end of perfectly smooth curvature. Finally, the two concentric tubes are bent together in the same shape as the holder *L* of Figure 1, bringing the opposite ends of the wires in an accessible position for contact. In combustion work a third gas holder is used to store the oxygen.

When the proper mixtures are ready for explosion the electrodes are placed at the top of the gas bubble to minimize the possibility of oxidizing the mercury. This brings the glass of the electrode holder above the mercury surface and undoubtedly introduces a small error due to the exchange of gases on the surface. An alternative method would be to place electrodes through the top of the gas holder, but because the smooth curvature of this is essential for the complete removal of gas, this method was not used.

Discussion of Results

In Table I are given a number of experimental results which were obtained by the procedure which has been described. It will be observed that the volumes used for analysis are from 500 to 1000 times less than those used in macroanalysis. It is possible to use a capillary buret of smaller diameter, and consequently to use smaller volumes for a determination, but it was felt that this would disproportionately increase the errors due to surface forces. Smaller volumes for analysis are not necessary in most photochemical work where high-intensity light sources are used.

It was found that the volume of oxygen necessary for complete combustion was at least double that theoretically required for the reaction. This need not be measured accurately in the analysis of a single hydrocarbon, such as methane, when the percentage is determined by absorption of the carbon dioxide produced in the explosion. In the analysis of a mixture of combustible gases, on the other hand, the exact volume of oxygen added must be known.

In macroanalysis the percentage of one combustible gas may be determined directly by obtaining the contraction in volume, assuming that the water vapor produced condenses until its vapor pressure at that temperature is reached and a correction made for this vapor pressure. That method was found not to apply in this work. In the combustion of hydrogen, for example, far more than enough water is formed than is theoretically necessary to saturate the residual oxygen. Nevertheless, consistent results could never be obtained until the water was removed by means of phosphorus pentoxide and the contraction in volume then read. Doubtless this was due to the surface of the glass adsorbing moisture to such an extent that the normal vapor pressure was never reached.

Although every gas used in these combustions was dried over either phosphorus pentoxide or calcium chloride, no difficulty which could be attributed to the lack of moisture was experienced in getting an explosion. The glass in this case probably furnished the moisture which is generally conceded necessary to catalyze the reaction.

In the mixtures of hydrogen and carbon monoxide no spark was used for the explosion. Attempts to explode this mixture quantitatively with the gases at room temperature were unsuccessful. However, upon increasing the temperature to approximately 300° C. the combustion was spontaneous and complete. The technic of this is simple. With the gases in a container ready for explosion, the flame of a minute gas and compressed-air torch is directed down on the top of the container. The gas bubble rapidly expands and, when its volume is approximately doubled, explosion occurs. Preliminary experiments with carbon monoxide and methane indicate that the carbon monoxide in this mixture may be determined successfully at 300° C. but that spontaneous explosion does not occur.

Note—Since submitting this article the authors have succeeded in selectively absorbing carbon monoxide in the presence of other combustible gases by using especially prepared solid silver oxide. The details of this method will be given in a subsequent paper.

The methane sample of Table I was prepared from calcium acetate and soda lime, washed with boiled water, and dried over phosphorus pentoxide, which is admittedly not a very satisfactory procedure. It is felt that the mean value of 97.4

per cent is probably nearer to the true value than is the theoretical 100 per cent. This idea is substantiated by the fact that, if 97.4 per cent is taken in calculating the theoretical per cent of methane in the hydrogen and methane mixture, it gives a value of 49.6 per cent, which is only 0.1 per cent lower than the mean of 49.7 per cent experimentally determined for this.

The theoretical purities of the other gases are considered to be correct.

The authors believe that Table I is representative of the degree of precision which is to be expected from this type of microanalysis. It is of the same general order as that of macroanalysis.

Acknowledgment

The first named author was the holder of the du Pont fellowship of the Department of Chemistry while this research was in progress and wishes to express his appreciation for this substantial aid.

Literature Cited

(1) Christiansen, *J. Am. Chem. Soc.*, **47**, 109 (1925); *Z. anal. Chem.*, **80**, 435 (1930).
(2) Dennis, "Gas Analysis," p. 371, Macmillan, 1920.
(3) Guye and Germann, *J. chim. phys.*, **14**, 194 (1916).
(4) Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912).
(5) Reeve, *J. Chem. Soc.*, **125**, 1946 (1924).
(6) Ryder, *J. Am. Chem. Soc.*, **40**, 1656 (1918).

Acid Value of Cellulose Fatty Acid Esters and Rapid Analysis of Certain Cellulose Acetates[1]

T. F. Murray, Jr., C. J. Staud, and H. LeB. Gray

Eastman Kodak Co., Rochester, N. Y.

Some of the more important methods to be found in the literature for the determination of the acetyl value of acetylated compounds have been critically reviewed. The method of Eberstadt has been found to be basically the best suited for work with acetylated cellulose, but it has been modified slightly in the interests of economy of material and time.

A method is described for the determination of acetic acid and formic acid in the presence of each other and in the presence of one or more acids not volatile with steam.

A method is proposed for the analysis of cellulose acetate by means of which the saponification time is cut from 24 hours to 1/2 hour, and the time of pretreatment is cut from 30 to 15 minutes. The results obtained by the method are in close agreement with those obtained by the slower method.

Suggestions are made for a method of precipitating the cellulose acetate in order to render it readily soluble in warm pyridine.

Some of the limitations of the pyridine method are indicated.

Since cellulose acetate was first prepared, and especially when cellulose acetates became of technical importance, the question of determining the acid values of the esters produced has been the subject of numerous investigations. The methods employed have fallen into two general classes: acid hydrolysis and saponification with alkali.

The acid hydrolysis was proposed by Ost in 1906 (*10*), and in the same year by Green and Perkin (*4*) who added alcohol, removed the ethyl ester by distillation, and saponified it with alkali.

The acid method has two major disadvantages: It is time-consuming and its accuracy is subject to question. The various processes calling for the distillation of ethyl acetate instead of acetic acid (*3*, *4*) were devised to increase the speed of the determination. Inaccuracies were due to the large amount of distillate that was required and the indefiniteness of the end point of the hydrolysis and distillation. Frequently the action of the strong acid on the cellulose residue produced formic acid which distilled with and was titrated as acetic acid. Sulfuric acid was commonly used to hydrolyze the cellulose ester, and the organic matter often resulted in the reduction of part of it to sulfur dioxide, causing high results.

Hess (*5*) continued to support the acid hydrolysis method and with some of his pupils has devised an elaborate system for buffering his sulfuric acid before distilling, and then carrying out the distillation under reduced pressure and also employing steam and hydrogen (*5*). There were, however, objections to the method, and the following year Weltzien and Singer (*14*) published a modification of it.

Cross and Bevan (*1*) proposed the use of sodium ethoxide for saponification, permitting the sample to stand at room temperature for 12 hours. Woodbridge (*15*) found that best results were obtained on standing for 16 hours, and Mork (*9*), on attempting to use higher temperatures to increase the rate of saponification, found that the effect of sodium ethylate as ordinarily used at refluxing temperatures, was to produce acid groups in the cellulose residue, thus causing high apparent acetic acid values. He proposed the use of a 0.5 *N* solution of sodium hydroxide in which the solvent is a mixture of equal parts of water and ethyl alcohol.

In 1909, too, Eberstadt (*2*), working under Knoevenagel, prepared a dissertation in which he showed that preliminary swelling of the acetate in alcohol-water or alcohol-acetone mixtures increased its porosity and facilitated saponification with 0.5 *N* potassium hydroxide. After that time, Knoevenagel (*6*) and his pupils did considerable work on the analysis of cellulose acetates.

Torii (*13*) compared the methods of Green and Perkin, Ost, Woodbridge, Barthelemy, Eberstadt, and Barnett. He concludes that Eberstadt's method is best in principle, but he recommends saponification with 1 *N* alkali for 1 hour at room temperature, a period which has been found to be far too short for some cellulose acetates.

Kruger (*8*) again reviewed the literature on the determination of the acetyl values of cellulose acetates and pointed out that for technical purposes the alkaline saponification is favored.

Technical control in the production of cellulose acetate made it necessary to select a method which would first give

[1] Received March 7, 1931. Communication 461 from the Kodak Research Laboratories.

reasonably accurate results, and second, would allow as large a number of samples as possible to be analyzed in a specified time.

Experimental Procedure

For the purpose of evaluating more critically the methods available at that time, the following experiments were carried out.

Refluxing the sample with 0.5 *N* sodium hydroxide for various lengths of time was tried, but the results obtained were irregular and unsatisfactory, as shown in Table I.

Table I—Acetyl Values Obtained by Refluxing Cellulose Acetate with 0.5 *N* Sodium Hydroxide

Hours	CH_3CO %
2	42.8, 43.1, 44.6, 43.5; av. 43.5
3	43.9, 44.9, 45.0, 45.1; av. 44.7
4	44.8, 44.4; av. 44.6
6	46.4, 45.5; av. 45.9
8	46.2
9	43.0

The same was true when the samples were saponified on a steam bath, indicated by the results given in Table II.

Table II—Acetyl Values Obtained by Heating Cellulose Acetate on Steam Bath with 0.5 *N* Sodium Hydroxide

Hours	CH_3CO %
2	42.6, 41.4; av. 42.0
2½	43.0, 42.1; av. 42.5
3	43.2
5	44.6, 42.0; av. 43.3
8	42.4
16	47.5
24	48.4, 47.9; av. 48.1
30	49.1
48	55.8, 54.6; av. 55.2

Experiments were run in which the sample, after refluxing in alkali for varying lengths of time, was acidified, the carbon dioxide boiled out, and the excess acid retitrated. The results so obtained also varied as Table III shows.

Table III—Acetyl Values Obtained by Refluxing Cellulose Acetate with 0.5 *N* Sodium Hydroxide and Correcting for Absorbed Carbon Dioxide

Hours	CH_3CO %
2	41.1
3	42.4, 43.8, 43.2, 40.7; av. 42.5
4	41.0
6	43.6, 42.2; av. 42.9
9	41.9

These data seemed to point to a reaction between cellulose and air, giving a compound which neutralized part of the sodium hydroxide. To investigate this, runs were made with filter paper and with cotton in which 0.5-gram samples of the material were refluxed for 3 hours with 20 cc. 0.5 *N* sodium hydroxide. One experiment with each material was refluxed in the usual way, a second was refluxed with an introduction into the reaction flask of a slow current of air, and a third was similarly treated but with hydrogen substituted for the air. The excess alkali was titrated back, and then the solution was acidified, the carbon dioxide boiled out under reflux, and the excess acid titrated back, giving the acetyl value corrected for carbon dioxide. The results are given in Table IV.

Table IV—Acetyl Values Obtained by Refluxing Filter Paper and Cotton with 0.5 *N* Sodium Hydroxide

Time, 3 hours; cotton, 99.5 per cent alpha cellulose

Procedure	Apparent Acetyl Value: Uncorrected % CH_3CO	Apparent Acetyl Value: Corrected for CO_2 % CH_3CO
FILTER PAPER		
Regular	3.4	2.6
With air	4.6	3.5
With hydrogen	2.7	2.5
COTTON		
Regular	6.2	5.4
With air	11.3	9.0
With hydrogen	...	5.7

Several runs were made in which cellulose acetate was saponified with 2 per cent sodium hydroxide, acidified with phosphoric acid, alcohol added, the ester distilled into standard alkali, and the amount of acetate in the original sample determined. The apparent acetyl values thus found varied and increased when darkening took place during distillation, as shown in Table V.

Table V—Acetyl Values Obtained by Refluxing Cellulose Acetate with 0.5 *N* Sodium Hydroxide, Adding Methanol and 10 cc. of 85 per cent Phosphoric Acid, Distilling into 0.5 *N* Sodium Hydroxide, Saponifying and Titrating Excess Sodium Hydroxide

Methanol Used *Cc.*	Acetyl Value % CH_3CO
35	36.2, 36.7; av. 36.4
75	40.7
65	41.7
115	42.6
225	42.9
125	43.4
200	43.9 46.6, 41.0; av. 43.8
250	44.9
150	46.6
300	49.5
250	47.6[b]
150	47.8[b]
150[a]	0.0[c]
150[a]	3.2[b]

[a] Purified Peruvian sliver. [b] Darkened. [c] Not heated to darkening

Eberstadt's method was investigated and found to be the most satisfactory. For convenience the proportions used were modified somewhat. Thus, instead of a 1.0-gram sample and 50 cc. of 0.5 *N* potassium hydroxide, a 0.5-gram sample and 20 cc. of 0.5 *N* sodium hydroxide were used. While this smaller sample gave a slightly larger margin of error, this was more than outweighed by the convenience gained. With the above proportions, duplicate runs can be made using no more of the cellulose acetate than would be required for a single determination by the original Eberstadt method, a given quantity of standard solutions would serve for two and one-half times as many determinations, and in the case of all technically usable cellulose acetates thus far examined, four samples can be titrated back with one filling of a 50-cc. buret. These time economies are important where a great many samples are being analyzed each day.

Details of Present Method for Use with Cellulose Acetate

The material to be analyzed is dried to constant weight at 105° C., and a 0.5-gram sample of the cellulose acetate is accurately weighed and put into a 250-cc. Erlenmeyer flask. To this are added 20 cc. of 75 per cent aqueous ethyl alcohol and the flask kept at 50° to 60° C. for ½ hour.[2] To each flask are then added 20 cc. of 0.5 sodium hydroxide, the flasks tightly closed with rubber stoppers and kept in the bath for 15 minutes longer, then at room temperature, with occasional shaking, for 24 hours, or 48 hours if the material is hard and horny. At the end of this time the sides of the flask are washed with 50 to 75 cc. of distilled water, 2 drops of 1 per cent phenolphthalein solution are added, and the excess alkali is titrated back. With some samples there is a tendency for the cellulose to retain some of the alkali after the solution becomes colorless. In such cases it is necessary to stopper the flask again and allow it to stand, adding standard acid from time to time until the solution shows no further tendency to become red. The acetyl (CH_3CO–) value of the sample is calculated from the following formula:

$$\% \, CH_3CO = \frac{0.0215 \times \text{cc. } 0.5 \text{ NaOH} \times 100}{\text{weight of sample}}$$

Table VI gives the analysis of several samples of cellulose acetate using the above method. The results were taken from among a great many analyses of commercial and experimental cellulose acetates with a maximum range of acetyl content.

[2] It has been found convenient to use a double-walled bath in which acetone is kept refluxing. In this way a temperature of 53° C. is maintained with a variation of not more than 1° C.

Table VI—Analysis of Cellulose Acetate Using Method Described

Sample	Acetyl % CH_3CO-	Sample	Acetyl % CH_3CO-
A	44.6 to 44.6	I	32.9 to 33.1
B	44.5 to 44.6	J	22.7 to 22.8
C	42.6 to 42.8	K	13.2 to 13.2
D	39.8 to 40.1	L	11.4 to 11.8
E	39.4 to 39.4	M	4.8 to 5.0
F	38.0 to 38.1	N	3.7 to 3.9
G	37.7 to 37.9	O	1.6 to 1.7
H	37.0 to 37.0		

The completeness of the saponification by this method is indicated by the following experiments:

Two 25-gram samples of cellulose acetates A and B were saponified by the above method and the residues filtered off, washed, and dried. Samples of this recovered material were then analyzed for acetyl by the above method with the results shown in Table VII.

Table VII—Analysis of Residue for Acetyl

Weight of sample, 0.5 gram

Residue	Sodium Hydroxide Used	Hydrochloric Acid Required for Back Titration
	Cc.	*Cc.*
Sample from A	19.90	19.90
Sample from B	19.90	19.86
Tissue paper control	19.90	19.91

While satisfactory results can be obtained in the analysis of acetone-soluble cellulose acetates by the alkaline saponification without a preliminary treatment with alcohol, this is not true of the triacetate, as the following results indicate.

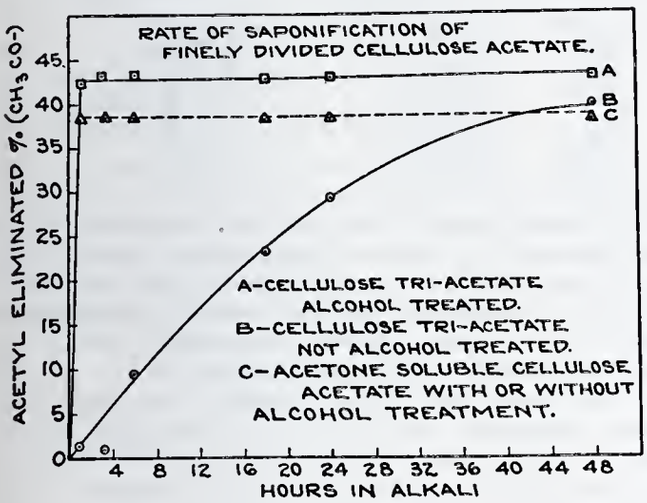


Figure 1

In Table VIII (see Figure 1) are given the rates of deësterification of very finely divided cellulose triacetate and of acetone-soluble cellulose acetate, both when pretreated with 75 per cent aqueous ethyl alcohol at 53° C., and when such treatment is omitted. Saponification was carried out at room temperature.

Table VIII—Deësterification Rates of Finely Divided Materials

Time of Saponification	Cellulose Triacetate Without alcohol	Cellulose Triacetate With alcohol	Acetone-Soluble Cellulose Acetate Without alcohol	Acetone-Soluble Cellulose Acetate With alcohol
Hours	% CH_3CO	% CH_3CO	% CH_3CO	% CH_3CO
1	1.3	42.4	38.5	38.3
3.5	0.9	43.3	38.5	38.5
6	9.5	43.3	38.5	38.3
18	23.2	42.8	38.3	38.1
24	29.2	43.0	38.1	38.1
48	39.6	42.8	38.1	38.1

When acetone-soluble cellulose acetate in the form in which it is usually employed in technical operations was used instead of the finely divided material on which Table VIII is based, saponification was very much slower, owing to the much smaller surface area exposed. Table IX gives the results of these analyses both when the sample is pretreated with 75 per cent alcohol and when this treatment is not used.

Table IX—Deësterification Rates of Acetone-Soluble Cellulose Acetate

Time of Saponification		Acetyl Eliminated Without pretreatment	Acetyl Eliminated With pretreatment
Hours	*Minutes*	% CH_3CO	% CH_3CO
1	15	..	36.7
1	25	33.6	..
2	35	37.2	..
5	15	37.2	..
17	30	..	39.7
23		39.8	..
24		..	39.6

These results are shown graphically in Figure 2.

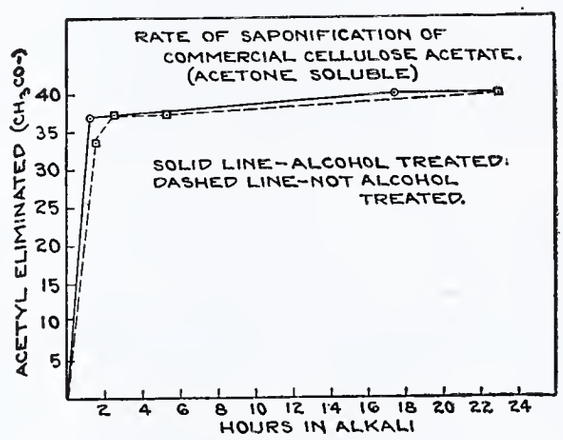


Figure 2

The saponification can be brought to completion more quickly if the samples are allowed to remain for a longer period at 53° C., as indicated by the fact that 39.1 per cent acetyl was eliminated in 1.5 hours at this temperature following pretreatment with alcohol. Long treatment at elevated temperatures is not recommended, however, owing to the tendency of the alkali to attack the cellulose under these conditions.

In the case of acetylated sugars, acetylated degradation products of cellulose, and cellulose mixed esters where one of the acid residues is formic or an acid not volatile with steam and the other is acetic or some other steam distillable acid, a modification of the above procedure may be successfully used. Direct titration of the excess alkali would not give a measure of the ester content in the case of esters of degraded cellulose and some sugar acetates, either because of the pronounced color developed in the presence of the alkali, or because of a reaction between the carbohydrate residue and the alkali which would give a high acid value. In the case of mixed esters, it is obvious that direct titration would not show the relative amounts of the various esters.

In such cases the saponification is carried on as above, and for mixed esters total acidity is determined by back titration. Any insoluble matter is filtered off, an excess of 30 per cent tartaric acid solution is added, the solution is transferred to a boiling flask connected for steam distillation, and the volatile acid or acids are distilled.

By maintaining a small volume, and therefore a high salt concentration in the distilling flask, the amount of distillate necessary to carry over all of the volatile acids is reduced to 2 liters as against 4 or 5 liters when considerable water accumulates. When 2 liters of distillate have been obtained, if no formic acid is present the distillate is boiled under reflux to free it of carbon dioxide, cooled with a soda lime tube in the condenser, the condenser washed out with distilled water, and the whole titrated to neutrality using phenolphthalein and standard alkali. A non-volatile acid would be obtained by difference.

In cases where formic and one other volatile acid are present together, the distillate is made alkaline with sodium

carbonate, evaporated on a steam bath to small volume, and the formic acid determined according to the method of Ost (*11*) in which an excess of standard potassium permanganate is added to the alkaline solution which is then heated to 60° C. for 5 minutes. It is acidified with dilute sulfuric acid, an excess of oxalic acid solution, which has been recently standardized against the potassium permanganate, is added, and the excess oxalic acid titrated back with standard potassium permanganate.

After the formic acid has been oxidized, the solution is made slightly alkaline with sodium hydroxide, an excess of tartaric acid solution is added, and the solution is again distilled at high concentration, collecting 2 liters. The carbon dioxide is boiled out as before and the other volatile acid is determined in the cooled solution. The results so obtained are accurate to within 0.5 per cent and easily reproducible.

Rapid Method for Acetyl Determination

While the method for acetyl determination given above is perfectly satisfactory for routine determinations, there are times when a much more rapid method would be desirable.

In the majority of methods proposed heretofore for the determination of acetyl content, it is apparent that the limiting factor in the rate of saponification of the cellulose acetate is the rate of diffusion of the alkali into the mass and the diffusion out of the saponification products. It has therefore appeared desirable to attempt determinations in highly dispersed phase systems. To this end a sample was dissolved in 20 cc. of acetone and to this were added 20 cc. of 0.5 *N* sodium hydroxide with gentle agitation. The sample was then let stand at room temperature. Table X gives the results obtained by this procedure.

Table X—Determination in Acetone

Time of Saponification	Acetyl Eliminated % CH_3CO
45 minutes	39.6
2 hours	39.4

A sample of the cellulose acetate was dissolved in acetone, and after the alkali was added the sample was held at 53° C. for $^1/_2$ hour. The acetyl value so obtained was 39.8 per cent.

From the above data it would appear that determinations made in acetone might be satisfactory for the purpose of plant control. The range of acetone solubility is, however, rather restricted, and a solvent which would have a wider range of solubility and which would not be affected by the alkali appeared to be more desirable. Pyridine answered the requirement of greater solubility range. To study the effect of alkali on acetone and on pyridine, 20-cc. portions of alkali were pipetted into each of six flasks. To two of these nothing was added, to two were added 20-cc. portions of acetone, and to the remaining two were added 20-cc. portions of pyridine (Eastman white label). After standing stoppered at room temperature for $1^1/_2$ hours, the alkali was titrated with 0.5 *N* hydrochloric acid, using phenolphthalein as an indicator. The amount of acid used was exactly equal to the amount of alkali in the blank and when pyridine was added, but the acetone samples required 0.10 cc. less acid than did the checks. To investigate further the effect of alkali on pyridine, 20 cc. of 0.5 *N* alkali were added to 20 cc. of pyridine and the solution was kept at 53° C. for 2 hours. The alkali was then titrated back and required 20 cc. of 0.5 *N* acid.

From the foregoing results it appeared that pyridine would be an ideal medium in which to carry out acetyl determinations. The method suggested below is devised for rapid determinations of acetyl content of cellulose acetate containing between 44 and 35 per cent CH_3CO.

The cellulose acetate is weighed out, using 0.5-gram portions, and transferred to Erlenmeyer flasks of 200 cc. or 250 cc. capacity. To each are added 20 cc. of Eastman pyridine. The flasks are covered with an inverted beaker, or loosely stoppered and warmed on a steam bath or in the 53° C. constant-temperature bath with occasional shaking until the cellulose acetate has completely dissolved. This should not require more than 15 minutes. To each flask are then added 20 cc. of 0.5 *N* sodium hydroxide, while shaking gently to disintegrate any precipitate that forms. The flasks are tightly stoppered with rubber stoppers and placed in the 53° C. constant-temperature bath for $^1/_2$ hour. At the end of this time the sides of the flask are washed with about 25 cc. of distilled water, two drops of phenolphthalein are added, and the excess alkali is titrated back with standard acid until the solution becomes just colorless. Using the pyridine method the tendency of the cellulose to retain alkali which diffuses out of the material slowly, thus delaying final back titration, is eliminated. This fact also increases the speed of the determination.

The acetyl value is calculated according to the formula given above. Table XI gives the results obtained when the pyridine method of analysis is used, as compared with the results obtained with 75 per cent alcohol pretreatment method and allowing the samples to stand at room temperature for 24 hours.

Table XI—Comparison of Acetyl Values Obtained by Pyridine and Eberstadt Methods

Sample Designated	Modified Eberstadt Method % CH_3CO	Pyridine Method % CH_3CO
38C–41	39.3, 39.7, 39.6, 39.3	39.8, 39.8
13770	43.5, 43.7	43.4, 42.8
14770 D	40.4, 40.4	40.2, 40.2
14770 K	35.9, 35.7	35.7, 35.9
50C–41	44.9, 44.7	44.7, 44.7, 44.7
5597	38.9, 38.7	38.7, 38.7
5633	37.8, 37.8, 37.8, 38.1	38.5, 38.1, 38.3, 38.1
5635	38.3, 38.3	38.1, 38.1
15881A	41.3, 41.3	41.1, 41.1
15881B	41.3, 41.3	41.3, 41.3

The range of acetyl values used with the pyridine method has been from the triacetate with an acetyl value of about 44.8 to an acetate which contained 35.8 per cent CH_3CO. On all of these materials covering a range of nearly 10 per cent CH_3CO, the method worked satisfactorily provided the conditions prescribed were rigidly adhered to.

An important factor in the procedure is that the cellulose acetate used must be in such a physical condition that it is easily and readily dissolved in warm pyridine. To accomplish this, the acetylation solution on which the analysis is to be made is diluted with two to four volumes of acetone and precipitated by pouring it, in a small stream, into six or eight volumes of hot water (85° to 95° C.). This gives a finely divided or fluffy precipitate, which dissolves readily and completely in pyridine even in the case of cellulose triacetate acetylation solutions. If the precipitate consists of large, hard nodules, the pyridine gelatinizes them without bringing them into solution and the results are low.

This is illustrated by the results obtained on a sample of precipitated cellulose triacetate. This acetate, by the modified Eberstadt method, gave values of 44.5, 44.7, 44.7, and 44.7 per cent CH_3CO. Samples of the same material heated with pyridine for 30 minutes on a steam bath then held at 53° C. for $^1/_2$ hour after the addition of the 0.5 *N* alkali gave 43.9 to 43.5 per cent CH_3CO. A sample given a pretreatment in pyridine for only 15 minutes gave a value of 42.8 per cent.

Upon long contact pyridine appears to react with the cellulose acetate, especially in the presence of sodium hydroxide. A sample treated as for the above method of analysis was saponified at 53° C. for 48 hours. The sample became brown and the end point was indefinite. A second sample of cellulose acetate was dissolved in pyridine and the solution held at 53° C. for 48 hours. The alkali was then added and saponification was carried on for $^1/_2$ hour at 55° C. The acetyl

value so obtained was 40.4 per cent, an increase of 0.6 per cent over the value obtained when the analytical procedure given was strictly followed.[3]

Literature Cited

(1) Cross and Bevan, Worden Tech. Cellulose Esters VIII, 2921.
(2) Eberstadt, Dissertation, Heidelberg, "Über Acetylcellulose," 1909.
(3) Freudenberg, *Ann.*, **433**, 230 (1923).
(4) Green and Perkin, *J. Chem. Soc.*, **89**, 811 (1906).
(5) Hess, Weltzien, and Messmer, *Ann.*, **435**, 64 (1924).
(6) Knoevenagel, *Chem.-Ztg.*, **35**, 248–9 (1922).
(7) Knoevenagel and König, *Cellulosechemie*, **3**, 113–21 (1922).
(8) Kruger, *Farben-Ztg.*, **35**, 2032 (1930).
(9) Mork, *J. Am. Chem. Soc.*, **31**, 1069 (1909).
(10) Ost. *Z. angew. Chem.*, **19**, 993 (1906).
(11) Ost, *Chem.-Ztg.*, **32**, 815 (1908).
(12) Schultze and Hess, *Ann.*, **450**, 65 (1926).
(13) Torii, *J. Chem. Ind. (Japan)*, **25**, 118–31 (1921).
(14) Weltzien and Singer, *Ann.*, **443**, 71 (1925).
(15) Woodbridge, *J. Am. Chem. Soc.*, **31**, 1068 (1909).

[3] Subsequent to the carrying out of this work, a procedure using pyridine was published by Battegay and Penche, *Bull. soc. chim.*, **45**, 132 (1929).

Determination of Phenols in Water Solution

Adaptation of Bromine Method to Include Range of 1 to 75 p. p. m.[1]

J. A. Shaw[2]

Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

Perhaps the most frequently used method for determining phenols in coke-plant effluents and similar process liquors is the bromine method. This method was not readily applicable to samples containing much less than 75 p. p. m. phenol. The present article describes a simple procedure making it applicable to the analysis of samples having a concentration of 1 p. p. m. phenols or even less. Lower concentrations than this in plant liquors are usually of little importance.

A RAPID method for the determination of phenols in solutions such as gas liquor was published by the writer in 1929 (*1*) and, from the testimony of many chemists using it, it appears to have given entire satisfaction when applied within the limits specified. However, the method without modification was not applicable to a sample containing less than 75 p. p. m. phenols. It is therefore evident that it is applicable to the most important of the phenol-bearing plant effluents, but that it is not satisfactory for the analysis of a large number of plant effluents containing perhaps only a few parts per million of phenols. At the present time the methods employed in analyzing these effluents for phenols are time-consuming and in some cases actually grossly inaccurate. For this reason it is believed that a real need exists for a rapid and reasonably accurate method for determining phenols in liquors having a tar acid concentration between 1 and 75 p. p. m. In the course of some work done in The Koppers Research Corporation Laboratories, this need became acute and a variation of the previously published method was developed to meet this situation.

The variation in procedure consists simply in concentrating the phenols into caustic soda solution by means of ether[3] [$(C_2H_5)_2O$] washes, heating the sodium hydroxide solution to drive off the ether (and certain other impurities) and then applying the previously published method of Shaw (*1*) to the acidified caustic solution.

Apparatus and Reagents

In addition to the apparatus and reagents originally specified, a separatory funnel for 1000 ml., and one for 100 ml., and U. S. P. ethyl ether $(C_2H_5)_2O$ are required.

Procedure

By means of a graduated cylinder, measure 800 ml. of sample into the large separatory funnel. Acidify with sulfuric acid. Add 125 ml. of ether, shake well, and allow to stand 2 or 3 minutes. Separate the two layers. Wash the aqueous layer twice more with 75-ml. portions of ether and combine the ether washes. Now discard the aqueous layer and place the ether in the separatory funnel.

Wash the ether three times with 8-ml. portions of 10 per cent sodium hydroxide solution and finally with one 10-ml. portion of distilled water, combining these aqueous alkaline washes. Boil gently to remove most of the ether, cool, and dilute to a volume of 50 ml. in a small graduated cylinder. In removing the ether from the caustic by boiling, the solution becomes first turbid and then clear, indicating the disappearance of most of the ether.

All of the phenol in the sample has now been concentrated into the 50 ml. of caustic solution. This may now be analyzed according to the previously published method if the concentration of phenol in the original sample was not less than 5 p. p. m. To save time it is well to take a few milliliters of the caustic solution, make just acid to methyl orange with sulfuric acid, and add two volumes of distilled water and a slight excess of bromine water in a small test tube. If a distinct turbidity is not produced, the phenol must be further concentrated. To do this, note the volume of the caustic solution, acidify with sulfuric acid, and repeat the previous procedure for concentrating with ether. In this case the small separatory funnel should be employed. Use three 10-ml. portions of ether and three 3-ml. portions of caustic, supplementing the caustic washes with one water wash of 3 ml. volume. The aqueous alkaline washes should be dropped directly into the 8 × 1 inch (20.3 × 2.5 cm.) test tube in which the final phenol distillation is to be made.

Calculations

Assume only one series of ether washes to have been made. Then

$$\frac{\text{p. p. m. phenol in standard matched} \times \text{dilution factor}}{\text{concentration factor}} = \text{p. p. m. phenol in sample}$$

For example, a 750-ml. sample was washed with ether and caustic solution as above described and the caustic diluted to exactly 50 ml. Ten milliliters were acidified and distilled, and 25 ml. of distillate were caught. When 10 ml. of dis-

[1] Received March 10, 1931.

[2] Industrial fellow, Multiple Fellowship of The Koppers Research Corp., Mellon Institute, Pittsburgh, Pa.

[3] The chemists of the U. S. Steel Corp. use ether for this purpose in a somewhat different connection.

tillate were diluted to 15 ml., they matched 30 p. p. m. standard upon bromination.

Then

$$\frac{30 \times 15 \times 25 \times 50}{10 \times 10 \times 750} = 7.5 \text{ p. p. m. phenol}$$

Discussion

By the procedure as outlined, solutions containing 1 p. p. m. of phenols or even less can be analyzed in 1 hour, and the error should be distinctly less than 10 per cent. The following results are some that were obtained on synthetic solutions:

PHENOL

In sample	Found
P. p. m.	*P. p. m.*
25.0	25.1
5.0	4.80
1.0	1.00

The ether, after having been thoroughly washed with both dilute caustic and acid, may be saved if desired and used for subsequent work.

In addition to making possible the rapid analysis of waters containing relatively low concentrations of phenols, this preliminary treatment renders the previously published method satisfactory for determining phenols in ammonia liquors dephenolized by immiscible solvents. For some reason not well understood by the writer, the bromine method as previously published failed to give good results on liquors dephenolized in this manner. It is the writer's opinion that this difficulty arose from the relatively large amount of thiosulfate which is usually formed when handling sulfide-bearing liquors in contact with air.

Literature Cited

(1) Shaw, J. A., IND. ENG. CHEM., Anal. Ed., 1, 118 (1929).

Determination of Organic Halogen by Liquid Ammonia-Sodium Process[1]

Thomas H. Vaughn and J. A. Nieuwland

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.

The liquid ammonia process for the determination of organic halogen has been modified so as to dispense with all special apparatus, to increase the accuracy, and to reduce the time required for a complete determination. By the modified method determinations are extremely simple, very accurate, and require in most cases only 20 to 40 minutes for completion.

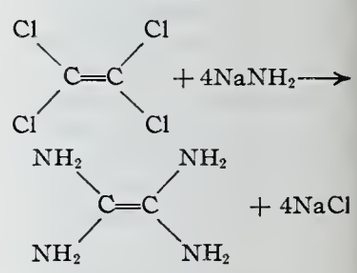
The modified method has been applied to the determination of organic fluorine and gives excellent results.

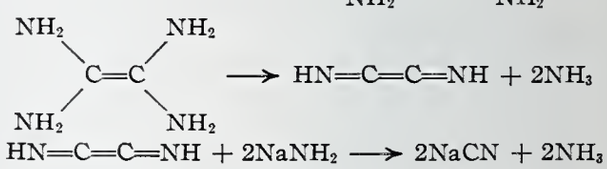
WHILE investigating the action of solutions of sodium in liquid ammonia on organic haloids, it occurred to the authors that since halogens were apparently quantitatively removed from all types of organic compounds, this method of treatment might be used as a basis for halogen determination. Such proved to be the case.

On looking up the literature, it was found that Chablay (*1*) had employed this reaction for the determination of organic chlorine, bromine, and iodine; and that Dains and co-workers (*2*, *3*) had used the method and investigated the possibility of error caused by cyanides produced during the decomposition.

According to the method described by Chablay, the substance is placed in a special reaction tube which is cooled in a bath of solid carbon dioxide and acetone. Ammonia is condensed in the tube and metallic sodium added. After completion of the reaction, the ammonia is distilled off and the halogen precipitated as silver halide. This method, while very rapid for compounds soluble in liquid ammonia, requires an hour or more for the decomposition of insoluble substances. With insoluble compounds, moreover, low results are usually obtained.

Dains and Brewster (*2*) investigated the action of sodium in liquid ammonia on organic compounds and examined the products of reaction for cyanide. They found that cyanides were produced from halogen compounds in only a few cases. It is interesting to note that in all of these cases two or more halogens were attached to a single carbon atom. In view of this fact, and since it is known that one of the principal products of the reaction of sodium in liquid ammonia on organic haloids is an amine, the production of cyanide in these special cases can probably be explained by the following set of reactions, using tetrachloroethylene as an example:





$$HN{=}C{=}C{=}NH + 2NaNH_2 \longrightarrow 2NaCN + 2NH_3$$

Similar equations can be written for all observed cases of cyanide formation.

In the procedure to be described, the original Chablay method has been modified in such a manner as to increase the rapidity and accuracy of analysis of insoluble materials and to do away with all special apparatus.

Modified Procedure

Fifty milliliters of liquid ammonia are run into a 400-ml. beaker and 0.1 to 0.4 gram of the halogeno-organic material added. If solution does not take place upon stirring, ether, monobutylamine, dimethyl acetal, or other organic solvent inert towards sodium in liquid ammonia is slowly added until the material is dissolved. One gram of freshly cut metallic sodium is then added in small pieces and the covered beaker allowed to stand until the reaction is complete (usually 30 seconds to 2 minutes). At this point the solution should have a persistent blue color of uniform depth. Five grams of ammonium nitrate dissolved in a few milliliters of liquid ammonia are now added to remove the excess sodium. The covered beaker is placed in a water bath at room temperature, and the solution allowed to evaporate to dryness (hood). The

[1] Received March 13, 1931.

solids are taken up in water, diluted to 150 ml., filtered if necessary, acidified with nitric acid, and treated with an excess of silver nitrate solution. The solution is boiled to coagulate the silver halide, filtered, and washed with water containing a few drops of nitric acid and then with acetone. The precipitate is dried at 135° C. for 15 minutes, and weighed.

The use of organic solvents reduces the time of reaction of insoluble substances remarkably and does away with low results by facilitating complete decomposition. With hexachloroethane, for example, the time of reaction was reduced from 90 to 2 minutes and the error was decreased from 0.42 to 0.07 per cent.

When the ammonia solutions are allowed to evaporate as recommended by Chablay, and the excess sodium destroyed by the addition of water, tars result in many cases. The addition of ammonium nitrate in liquid ammonia before evaporation obviates this.

When solids are being analyzed, the beaker containing the material should be cooled by placing in a shallow dish containing a layer of about 0.5 cm. of liquid ammonia, before the solvent ammonia is added. This avoids the violent spattering caused by the rapid vaporization of the ammonia on contact with the bottom of the beaker.

Volatile liquids can be weighed in thin-walled glass bulbs which are then broken under liquid ammonia in a beaker. After decomposition, evaporation, and addition of water, the solution can be decanted from the glass fragments and analyzed in the usual manner.

In some cases organic solids are produced during the decomposition. These must either be filtered off or put in solution by the addition of aldehyde-free acetone or other suitable solvent before precipitation of the halide.

In an attempt to speed up the determination, volumetric methods were tried. The Fajans method, using sodium eosin as an indicator, was found to give satisfactory results, since the titrations can be made in acid solutions. All volumetric determinations reported were made by this method. The Volhard method also gives excellent results.

The modified method was tried on a micro scale and gave good results. Samples containing 16 mg. of 3,5-dibromo-2-aminobenzoic acid were decomposed, taken up in water, and titrated by the Fajans method with 0.01 *N* silver nitrate solution. Bromine calculated was 57.15 per cent; bromine found, 57.39 per cent; difference, 0.24 per cent.

Results of analyses of chloro, bromo, and iodo compounds are given in Tables I, II, and III, respectively. All percentages given are the average of at least two determinations.

Table I—Analyses of Chloro Compounds

Compound	Chlorine Present	Chlorine Found	Difference
	%	%	%
Trichloroacetic acid	65.11	65.19	0.08
Chloral hydrate	64.33	64.21	0.12
Hexachloroethane	89.86	89.91	0.05
Chlorobenzene	35.56	35.56	0.00
p-Dichlorobenzene	48.28	48.23	0.05
Hexachlorobenzene	74.73	74.80	0.07
2,4,5-Trichloroacetanilide	44.62	44.55	0.07
Chlorophenylpyrazolone	18.23	18.19	0.04
1-Chloro-2-methylanthraquinone	15.25	15.20	0.05

Table II—Analyses of Bromo Compounds

Compound	Bromine Present	Bromine Found	Difference
	%	%	%
Ethyl bromide[a]	73.37	73.46	0.09
3,5-Dibromobenzoic acid	57.15	57.00	0.15
Styrene dibromide[a]	60.56	59.95	0.61
Dibromoisatin	52.46	52.55	0.09
1,3-Dimethyl-5-bromofluorobenzene	39.37	39.42	0.05

[a] Volumetric determination.

In Table I analyses of three compounds which contain three halogens to a single carbon atom are given. Inasmuch as Dains and Brewster (*2*) reported cyanide production from this class of compounds, it must be assumed that any silver cyanide precipitated was decomposed by the action of dilute nitric acid during the coagulation of the silver chloride, or that in the presence of an organic solvent cyanide formation is inhibited.

Table III—Analyses of Iodo Compounds

Compound	Iodine Present	Iodine Found	Difference
	%	%	%
n-Butyl iodide	68.98	68.86	0.12
Methylene iodide	94.77	94.84	0.07
Phenyl iodide	62.23	62.23	0.00
Tetraiodophthalic anhydride[a]	77.91	77.08	0.83

[a] Volumetric determination.

The agreement between duplicate analyses of the same sample of various halides is shown in Table IV.

Table IV—Agreement of Analyses

Compound	Sample I	Sample II	Difference
	%	%	%
p-Dichlorobenzene	48.17	48.28	0.11
Chlorophenylpyrazolone	18.25	18.13	0.12
Methylene iodide	94.77	94.91	0.14
1,3-Dimethyl-5-bromofluorobenzene	9.33	9.27	0.06
2-Fluoroanthraquinone	9.13	9.27	0.14

Analysis of Fluoro Compounds

There seems to be, so far as we know, no completely satisfactory method available for the determination of organic fluorine.

It has been found that sodium in liquid ammonia reacts quantitatively with fluoro organic compounds to form sodium fluoride and this reaction has been applied to the determination of organic fluorine.

The material containing fluorine is decomposed by the modified procedure given above. The decomposition products are taken up in hot water to which 5 grams of ammonium nitrate have been added, and the fluorine ion precipitated by the addition of an excess of hot calcium nitrate solution. The precipitate is digested for 30 minutes, cooled, filtered on a Gooch crucible, washed with water and acetone, dried at 180° C., and weighed. The volume of wash water used is measured and the weight of precipitate corrected for the solubility of calcium fluoride.

Cyanides cannot interfere in the determination of fluorine, since calcium cyanide is soluble.

Results of analyses for fluorine are given in Table V. These results are, like those in Tables I, II, and III, the average of at least two determinations.

Table V—Analyses of Fluoro Compounds

Compound	Fluorine Present	Fluorine Found	Difference
	%	%	%
Fluorobenzene	19.79	19.78	0.01
p-Fluoronitrobenzene	13.47	13.28	0.19
1,3-Dimethyl-5-bromofluorobenzene	9.36	9.30	0.06
o-Chlorophenylfluoroform	31.58	31.36	0.22
2-Fluoroanthraquinone	9.06	9.20	0.14

Fluorine and bromine were both determined on the same sample in the case of 1,3-dimethyl-5-bromofluoro benzene. The fluoride was first precipitated and the bromide determined in the filtrate.

Acknowledgment

The writers are indebted to Roger Adams of the University of Illinois, and to the Jackson Laboratory, E. I. du Pont de Nemours and Co., for a number of the compounds on which this method was tested.

Literature Cited

(1) Chablay, *Ann. chim.*, [9] **1**, 510 (1914).
(2) Dains and Brewster, *J. Am. Chem. Soc.*, **42**, 1573–9 (1920).
(3) Dains, Vaughan, and Janney, *Ibid.*, **40**, 936 (1918); see also Clifford, *Ibid.*, **41**, 1051 (1919).

Method for Analysis of Volatile Compounds Containing Carbon, Hydrogen, and Nitrogen[1]

W. Scholl and R. O. E. Davis

Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

A method of analysis for mixtures of gases containing ammonia, carbon dioxide, and water vapor has been developed using solid absorbents whereby small samples of a few milligrams may be analyzed accurately by measurement of volumes at reduced pressures.

The method was also employed to determine nitrogen, hydrogen, and carbon in volatile organic materials whose products of combustion are composed of water vapor, carbon dioxide, and nitrogen.

The method can be employed with accuracy where samples are too small to obtain accurate results by the ordinary method of determining the increase in weight of absorptive materials.

A description of the apparatus is given and the method of procedure in analyzing gases and liquids is outlined.

In a study of the vapor pressure of the system urea-water-ammonia-carbon dioxide it became necessary, in order to determine the partial pressure of the constituents in the gas phase, to develop a method of analysis for small quantities of gas containing carbon dioxide, ammonia, and water vapor. Since the total volume of gas available for analysis was often between 2 and 4 cc., it was found necessary to adopt a microanalytical method, after a number of tests had been tried using the ordinary absorption chain.

The method finally adopted was based on the principle of the method described by Hackspill and d'Huart (*2*), but modified to suit the purpose of our investigation. While developed for use in analyzing a gas containing ammonia, carbon dioxide, and water vapor, it was also employed in test runs for the determination of the carbon, hydrogen, and nitrogen content of several volatile compounds containing these elements. Since the beginning of this work somewhat similar methods of analysis for small quantities of gas have been described by Prescott (*4*) and Ambler (*1*).

Principle of Method

The principle of the modified method is combustion of a known volume of gas in the presence of copper oxide, and the determination of the volumes of nitrogen, carbon dioxide, and water, of which the gas is composed after the combustion. The water was absorbed by phosphorus pentoxide and the combined volumes of carbon dioxide and nitrogen determined. Then the carbon dioxide was absorbed by potassium hydroxide and the volume of nitrogen remaining was measured. The water was determined as the difference between the original volume of gas taken and the sum of the volumes of carbon dioxide and ammonia (equivalent of the nitrogen volume). The determination of water by absorption in phosphorus pentoxide differed from the method of Hackspill and d'Huart in that they separated the water by freezing it out at −80° C., and determined its amount from the volume of hydrogen produced on allowing the water to react with calcium hydride. The absorption of water by phosphorus pentoxide was a simpler procedure and gave satisfactory results.

Description of Apparatus

The apparatus is shown in Figure 1. The functions of the indicated units and their arrangement are as follows:

The sample of gas for analysis is introduced at *A* and is condensed in unit *B* at the temperature of liquid air.

The condensate may be expanded to vapor in units *C*, *D*, and *E*. Unit *D* is an 80-cm. mercury manometer, and *C* and *E* are calibrated bulbs with a total capacity of 600 and 150 cc., respectively. The bulbs are surrounded by water jackets whose temperature is controlled by circulating water from a constant-temperature bath. The total volume of the bulbs is such as to permit expansion of the gases to a pressure considerably less than the vapor pressure of the material to be analyzed, to prevent condensation on the walls of the bulbs.

Combustion of the gases is carried out at 550° C. on oxidized copper gauze contained in the first quartz tube of unit *G*. A second quartz tube containing reduced copper gauze is utilized to take up free oxygen and to reduce any oxides of nitrogen that might be formed in the first tube. Clear quartz tubes permitted inspection of the gauze to determine its condition. The tubes are 350 mm. long and 13 mm. inside diameter. The gauzes in the first and second tubes are 120 and 90 mm. in length, respectively. Two independently controlled electric furnaces are employed to heat the tubes.

Two glass bulbs, *F* and *I*, about 25 mm. in diameter, by alternate immersion in liquid air permit the passage of the gases back and forth through the heated tubes. This insures complete combustion of the gases.

Absorption of water vapor is accomplished by means of a U-tube, *J*, about 250 mm. long and 10 mm. inside diameter, containing a mixture of phosphorus pentoxide and pumice stone.

The bulb *K*, in conjunction with bulb *I* and similar to it, is useful in drawing the gases back and forth through *J* in a manner similar to that explained above.

By means of a Töpler pump, *L*, the gases are transferred to tube *N* through a capillary tube, *M*, of 0.5-mm. bore. The lower end of the capillary is sealed into the bulb *R* and bent upwards in the mercury. The volume of the pump is about 600 cc. and the ratio of its volume to that of the apparatus to be evacuated is about 3 to 1. Compressed air is used to lift the mercury from the lower bulb. The ground glass valve *Q* acts as a check valve to prevent mercury from passing back into the apparatus.

The gases are collected for measurement in tube *N* which is about 80 cm. long and of 8 mm. bore. Parallel to *N* and connected to it through a three-way stopcock, V_8, is a tube, *O*, of the same dimensions. The two tubes are mounted in front of a calibrated white glass millimeter scale, and the whole unit surrounded by a water jacket through which is circulated water from the constant-temperature bath. The volume of tube *N* was determined carefully to within 0.01 cc. for each 10-mm. length indicated on the scale. Tube *O* is used in conjunction with tube *N* to determine the pressure of the gases collected in tube *N*. Both tubes are connected through V_8 to a mercury leveling bulb.

The U-tube *P*, containing lump potassium hydroxide, is used for absorption of carbon dioxide.

The unit *H* is used for introducing samples of liquid mate-

[1] Received March 16, 1931.

rials in the study of the accuracy of the analytical method, liquids being more readily obtained in pure form and easily weighed in small capillaries in a manner similar to that described by Pregl (*3*). A ground glass cap closes one end, and this may be removed for introducing the sample in a sealed capillary. Stopcock V_{12} is used to break the capillary tubes, and stopcock V_{11} prevents the entire apparatus from becoming filled with air when inserting the capillary.

The entire apparatus with the exception of the two quartz tubes mentioned is made of Pyrex glass. The glass stopcocks are lubricated with a specially prepared grease made according to the directions given by Shepherd and Ledig (*5*). It is very necessary that this grease be of the proper consistency and exert no appreciable vapor pressure. The apparatus was connected to Hi-Vac and mercury vapor pumps, which were used to evacuate it previous to each experiment.

Experimental Procedure

In making an analysis the entire apparatus is first completely evacuated, precaution being taken to heat the copper gauzes to 800° C. and to pass a small Bunsen flame over the tubing to drive out moisture and volatile gases, else the volume measurements will be too large. Units *C*, *D*, *E*, and the tubing to stopcock V_2 are filled with mercury; then with *B* immersed in liquid air, the gas to be analyzed is condensed in this unit.

With stopcock V_2 closed, the unit *B* is allowed to warm up to room temperature and then the gas is expanded into units *C*, *D*, and *E*, with the total pressure adjusted by means of the mercury leveling bulbs to between 50 and 60 mm. of mercury. Finally, immersing *B* in boiling water and filling the unit from *B* to stopcock V_3 with mercury completely transfers all the gas to *C*, *D*, and *E*. The pressure, temperature, and total volume are determined.

A known volume of gas from *E* is transferred to bulb *F* by immersing the latter in liquid air. The gas is then completely oxidized by passing over the heated copper oxide several times, alternately immersing *F* and *I* in liquid air. While one bulb is immersed in liquid air, precaution should be taken to warm the other bulb and tubing with a small gas flame.

After oxidation of the gas is complete, the stopcocks V_6 and V_{10} are closed and V_5 is opened, permitting the products of combustion, water, carbon dioxide, and nitrogen, to come in contact with the phosphorus pentoxide. By immersing bulbs *K* and *I* alternately in liquid air, the gas is drawn back and forth over the phorphorus pentoxide, insuring the absorption of all water. The residual gas containing carbon dioxide and nitrogen is now collected in *N* by operating the Töpler pump until no appreciable quantity of gas is removed from the combustion part of the apparatus in a single operation of the pump.

The volume of the nitrogen–carbon dioxide mixture in *N* is determined at a given temperature and reduced pressure. On opening V_9, the carbon dioxide is absorbed by holding the gas in contact with potassium hydroxide. The residual nitrogen is again collected in tube *N* by operating the mercury pump, and its volume, pressure, and temperature determined.

From the volume of nitrogen measured, the equivalent volume of ammonia is computed. The difference between the total volume of gas sample and the sum of the volumes of ammonia plus carbon dioxide is a measure of the water present. All volumes are calculated to 0° C. and 760 mm. of mercury.

In the analysis of liquid samples, the procedure is the same as with gas samples with the exception of a difference in the manner of introducing the sample to the apparatus. The liquid to be analyzed is filled into thin capillaries of known weight, about 1-mm. bore, and 20 mm. in length. After sealing, the capillaries are reweighed to determine the weight of sample introduced. With stopcock V_{11} closed, a capillary containing a known quantity of sample is introduced into unit *H* and supported in such a way that one end just enters the bore of the plug in stopcock V_{12}. The end of the unit is closed by a ground glass cap and, after opening V_{11}, the apparatus, including the combustion and absorption units, is evacuated. Then stopcock V_{12} is turned sufficiently to break the capillary and release the liquid. The vapors produced are oxidized and the analysis carried out, as already described, for the amount of water, carbon dioxide, and nitrogen.

Results

A number of determinations using the method described were made of different materials, including liquids that readily vaporize or are gaseous at ordinary temperatures, and of the gas phase over a solid with considerable vapor pressure. The materials used were acetonitrile, $CH_3.CN$, b. p. 81.5° C.; acetone, $(CH_3)_2CO$, b. p. 56.1° to 56.2° C.; ammonium bicarbonate, NH_4HCO_3; and a mixture of ammonia and carbon dioxide. The results obtained are shown in Table I. In the

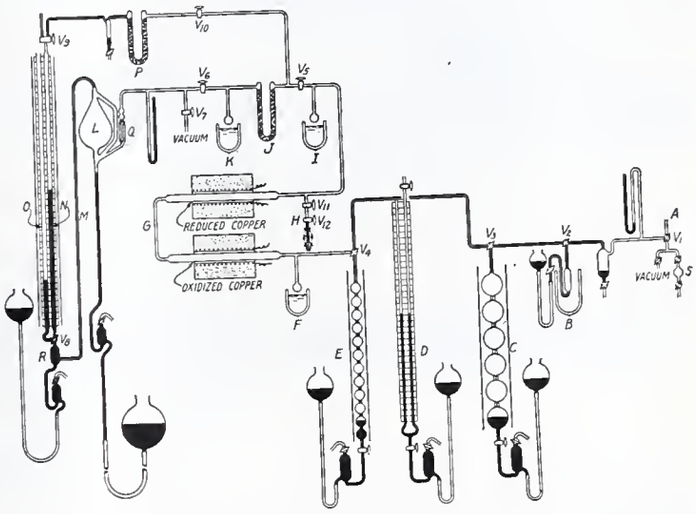


Figure 1—Apparatus for Determination of Carbon, Hydrogen, and Nitrogen in Gaseous or Volatile Compounds

case of ammonium bicarbonate, the gas sample was taken from the gas phase in equilibrium with the solid at the temperature of 30° C. With the mixture of ammonia and carbon dioxide, the pressure was kept low enough (about 6 cm. at 30° C.), in measuring the initial gas volume in unit *E*, not to cause condensation of ammonium carbamate. The acetonitrile and acetone samples were specially purified by redistillation; the ammonium bicarbonate was freshly prepared from purified carbon dioxide and ammonia; and the carbon dioxide and ammonia were of known purity.

Table I—Determinations on Materials of Known Composition

Materials	Weight of Sample	Component Determined	Amount Calcd.	Amount Determined
	Mg.		%	%
Liquids				
Acetonitrile (CH_3CN)	4.7	N_2	34.1	34.1
		C	57.5	57.5
		H_2	6.4	6.4
Acetone $(CH_3)_2CO$	8.3	C	62.0	61.5
Vapor in equilibrium with solid ammonium bicarbonate	15.2	NH_3	21.5	21.7
		CO_2	55 7	55.3
		H_2O	22.8	23.0
Gas mixture Ammonia + carbon dioxide	7.4	NH_3	53.5	53.9
		CO_2	46.5	46.1

The method of calculation may be illustrated by employing the results obtained in the analysis of the gas in equilibrium

with solid ammonium bicarbonate. The volume of the sample of gas taken is measured at a given pressure and temperature. The combustion of the gas has the effect of producing one volume of nitrogen for two of the volumes of ammonia according to the equation

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

Hence the volume of nitrogen obtained represents twice that volume of ammonia in the original sample. The volume of carbon dioxide is not changed during combustion, whereas the original volume of water is increased by the water derived from the oxidation of ammonia. This increased water volume is of no consequence in the analysis, however, since all the water is absorbed by phosphorus pentoxide before measuring the carbon dioxide and nitrogen. The volume of water in the original sample is determined as the difference between the volume of the original sample and the sum of the volumes of carbon dioxide measured directly, and of ammonia calculated from the measured nitrogen. All volumes are reduced to 0° C. and 760 mm. of mercury by use of the gas law equation

$$V_0 = \frac{273\ pv}{760(t + 273)}$$

where p = pressure of gas in mm. of mercury
v = volume in ml.
t = temperature in ° C.

The weights in grams of the gases were calculated from the volumes V_0 by the equation

$$W = \frac{V_0 \times \text{mol. wt. of gas}}{22400}$$

Table II is a sample data sheet on the ammonium bicarbonate determination.

Table II—Test on Ammonium Bicarbonate Vapor in Equilibrium with Solid Ammonium Bicarbonate

	Vol.	Pressure	Temp.	Vol.[a]	Weight	Amount Determined
	Ml.	*Mm.*	*° C.*	*Ml.*	*Mg.*	*%*
Vapor sample	66.34	53	29.9	4.32	15.2	
Analysis:						
$N_2 + CO_2$	6.14	295.5	30.6	2.15		
N_2	4.71	130.3	30.7	0.73		
Experimental results:						
NH_3 = (2 × 0.73)				1.46	3.3	21.7
CO_2 = (2.15–0.73)				1.42	8.4	55.3
H_2O = [4.32 − (1.42 + 1.46)]				1.44	3.5	23.0
Total				4.32	15.2	
Calcd. values:						
NH_3						21.5
CO_2						55.7
H_2O						22.8

[a] At 0° C. and 760 mm. pressure.

Although the method described has been employed on volatile or gaseous compounds whose products of combustion consist of water, carbon dioxide, and nitrogen, it was developed for the analysis of a gas composed of ammonia, carbon dioxide, and water vapor in determining the partial pressures of these constituents.

Literature Cited

(1) Ambler, H. R., *Analyst*, **54**, 517 (1929).
(2) Hackspill, L., and d'Huart, G., *Ann. chim.*, [10] **5**, 96–107 (1926).
(3) Pregl, F., "Quantitative Organic Microanalysis," pp. 62–65, Blakiston, 1924.
(4) Prescott, C. H., Jr., *J. Am. Chem. Soc.*, **50**, 3237–40 (1928).
(5) Shepherd, M., and Ledig, P. G., Ind. Eng. Chem., **19**, 1059 (1927).

Determination of Sodium in Organic Compounds

Use of Uranyl Acetate Method[1]

D. L. Tabern and E. F. Shelberg

Abbott Laboratories, North Chicago, Ill.

A modified uranyl acetate method has been applied to the analysis not only of alkali barbiturates, but also of other typical organic sodium salts.

Results thus obtained substantiated by other studies, particularly in the field of electrometric titrations, lead to the conclusion that the commonly accepted sodium sulfate method is not applicable to the analysis of certain alkali barbiturates.

During the course of an extensive study of the salts of certain newly synthesized barbiturates (*6*), the commonly accepted sodium sulfate (sulfated ash) method was found to yield very unsatisfactory results in the case of sodium ethyl-(1-methylbutyl) barbituric acid (Nembutal). Not only did the results vary from determination to determination, but average values were sometimes as much as 1 per cent below the expected. Variations in the technic of analysis, as well as in the mode of synthesis of the salt, failed to bring improvement.

Investigation demonstrated that at least two other analogous salts, sodium ethyl-*sec*-butyl- and sodium ethylisoamyl-barbituric acid (sodium Amytal), behaved in somewhat the same way. This was doubly surprising in view of the fact that the sodium sulfate method has long been employed for the analysis of sodium barbital, sodium Neonal, (sodium ethyl-*n*-butyl-barbituric acid), etc., and had just been made the official method for the analysis of sodium Amytal, one of the compounds in question (*4*).

After the conclusion of most of the work described subsequently, it was found that if all organic matter is removed from the barbiturate solution by acidification and extraction, sulfated ash determinations upon the filtrate yield the expected values. The reason for the interference of the organic portion of the molecule in the above instances is not clear. Such a modified sodium sulfate method is too cumbersome for general use and distinctly inferior to several methods to be described.

Methods Employed

Efforts were first directed toward the establishment of the purity of the various samples of Nembutal at hand. Both loss on drying *in vacuo* at 120° C. and extractable barbituric acid were found to be negligible. Nitrogen determined by the Kjeldahl method checked theory closely (found, 11.27 and 11.16; calculated, 11.3). Determination of the barbituric acid content by decomposition of the salt with dilute sulfuric acid and extraction yielded very close to the calculated amount.

Further confirmatory evidence was supplied by pH determinations. Five per cent solutions of several lots of carefully purified Nembutal gave values ranging from 9.6 to 9.75, as did a synthetic solution made from ethyl-(1-

[1] Received March 16, 1931.

methylbutyl-) barbituric acid and the calculated quantity of sodium hydroxide. Addition of but one-half the amount of barbituric acid necessary to account for the observed low sodium values gave a pH at least one-half a unit lower, and the solution soon reprecipitated free acid.

Christensen (*3*) has suggested the titration of alkali barbiturate salts with hydrochloric acid employing methyl red as an indicator, while a similar method to be found in German Pharmacopeia VI and Farmakopén Svenska, 1925, employs methyl red. Each of these titrations gave in our hands consistent results distinctly higher than the sodium sulfate method. To eliminate entirely the question of correct end point, and to be able to follow closely the entire course of the reaction, recourse was had to electrometric titration. Either the hydrogen or the quinhydrone electrode may be employed, and the sharpness of the break in the titration curve, Figure 1, leaves little to be desired. Briefly 0.4 gram of the alkali barbiturate is dissolved in from 50 to 75 cc. of water and titrated with 0.1 *N* hydrochloric acid. At a certain stage (about 12 cc. with Nembutal) the liberated barbituric acid separates, temporarily changing the contour of the titration curve. At the end point, 0.1 cc. produces a pH change of several units. The entire determination need not require more than 15 minutes.

The method served so satisfactorily that it was employed upon at least two samples of each of seven barbituric acid salts with the results summarized in Table I. Not only in the instance of Nembutal, but also in the cases of sodium Amytal and sodium *sec*-butylethyl-barbituric acids, the values obtained lie close to the calculated and distinctly higher than those secured with the sodium sulfate method.

Table I—Comparison of Results of Various Methods

Barbiturate	Calcd. Sodium	Sodium Sulfate	Electrometric Titration	Uranyl Acetate
Sodium barbital	11.1	10.82	11.0	11.13
Sodium phenobarbital	8.95		9.1	8.82
Sodium neonal	9.8		9.9	9.6
Sodium *sec*-butyl ethyl (A)	9.8	9.23	9.55	
Sodium *sec*-butyl ethyl (B)		9.31	9.60	9.61
Sodium amytal	9.3	8.98	9.02	
Sodium ethylmethylhexylcarbinyl	7.94	7.89	7.81	7.86
Nembutal A	9.3	8.4		9.09
Nembutal B	9.3	8.3	9.10	9.18
				9.12
Nembutal C	9.3	8.9		
			9.01	9.2
Nembutal D	9.3	7.7	9.32	9.25

Within the past three years, several methods have been developed (*1*, *2*, *5*) involving the quantitative precipitation of sodium as complex uranium-sodium-magnesium and uranium-sodium-zinc salts. To the best of our knowledge, these methods have not been previously applied to the analysis of organic compounds. In our hands, the following modification of the method of Kahane has given excellent satisfaction in the determination of sodium in a number of samples of seven typical barbiturates (see Table I). Its chief advantages are: (1) Rapidity. An entire gravimetric determination may be carried out in 2 hours. (2) Accuracy. One milligram of sodium gives 15 mg. of precipitate, allowing the use of small quantities of material. (3) Convenience. Ignition is not required; a number of analyses may be carried out at once; the precipitate may be weighed directly, determined colorimetrically or titrated; the presence of a moderate amount of potassium does not interfere.

About 0.1 gram of sample (containing from 5 to 20 mg. of sodium) is dissolved in 5 to 10 cc. of water or alcohol and to this is added 3 cc. of the following stock reagent for each milligram of sodium expected:

	Grams
Cryst. uranyl acetate	32
Magnesium acetate	100
	Cc.
Acetic acid	20
Alcohol (90%)	500
Water to make	1000

Filter at 20° C. before use.

The beaker is placed in ice water for one-half hour with occasional stirring, the precipitate transferred to a Gooch crucible, washed first with 5 to 10 cc. of precipitating solution, and finally with 95 per cent alcohol. When dried at 105° C., the precipitate has the composition

$$3(CH_3CO_2)_2UO_2 + (CH_3CO_2)_2Mg + CH_3CO_2Na + 6.5H_2O$$

and each gram is equivalent to 0.0153 gram of sodium.

The sodium analyses obtained by the above uranyl acetate method with Nembutal, and all of the other barbiturates studied are again all in very good accord with the calculated values, giving further proof that the direct sodium sulfate method is not applicable to the analysis of the products in question.

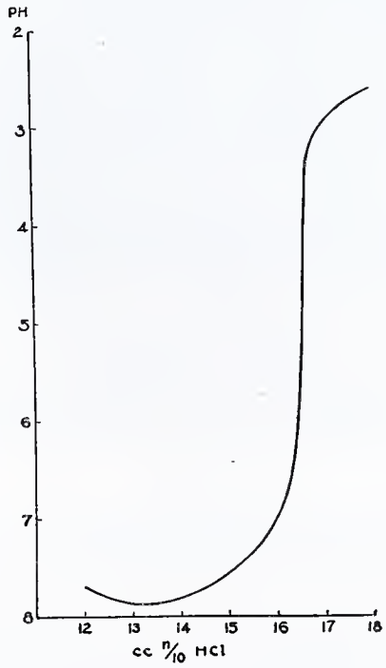


Figure 1—Titration Curve

To test further the applicability of the uranyl acetate method to various types of organic salts, particularly those of pharmaceutical interest, it has been employed in the analysis of the compounds listed in Table II. While of but a preliminary nature, the results indicate the value of the method and suggest the desirability of its further application in organic analysis.

Table II—Determination of Sodium in Various Organic Salts

Sodium Salt	Calcd.	Found
	Cc.	*Cc.*
Cinchophen	8.50	8.69
Benzoic acid	15.97	16.15
Tetraiodophenolphthalein	5.20	5.27
Formic acid	33.8	33.95
Potassium tartrate	8.15	7.85

Literature Cited

(1) Barber and Kolthoff, *J. Am. Chem. Soc.*, **50**, 1625 (1928).
(2) Caley and Foulk, *Ibid.*, **51**, 1664 (1929).
(3) Christensen, *Arch. Pharm.*, **267**, 598 (1929).
(4) Council on Chemistry and Pharmacy, *J. Am. Med. Assocn.*, **95**, 1178 (1930).
(5) Kahane, *J. pharm. chim.*, **11**, 425 (1930).
(6) Volwiler and Tabern, *J. Am. Chem. Soc.*, **52**, 1676 (1930).

Application of Oxalic Acid–Uranyl Acetate Actinometer to Measurement of Sunlight Intensity in Connection with Photochemical Changes in Gasoline[1]

L. C. Beard, Jr., and O. M. Reiff[2]

General Laboratories, Standard Oil Company of New York, 230 Park Ave., New York, N. Y.

A method for determining the stability of gasoline in sunlight of varying intensity and at various temperatures is described. This method permits a comparison to be made on the stability of gasoline under different climatic conditions and at different times of the year.

THE increasing use of visible pump bowls has made the light stability of gasoline a matter of considerable importance. In addition some refiners have used the formation of color in gasoline, exposed to sunlight for a definite period of time, as a measure of its color stability under ordinary storage conditions in the dark.

It is obvious, of course, that the development of color in gasoline during exposure to sunlight is dependent on three factors: first, the length of the time of exposure; second, the intensity of the sunlight; and third, the temperature of the gasoline during exposure. In the past, little attention has been paid to the last two factors, and the usual procedure for measuring the sunlight stability of gasoline has been to expose the gasoline for a definite period of time to bright sunlight and note the development of color which occurred during such exposure, with little regard to the sunlight intensity or the temperature of the gasoline.

In this paper is described an adaptation of the oxalic acid–uranyl acetate actinometer (*2*) suitable for the measurement of sunlight intensity in connection with the evaluation of the sunlight stability of gasoline.

Procedure

An oxalic acid–uranyl acetate solution is used which has the following composition: 6.30 grams of c. p. oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) per liter of solution and 0.2121 gram of c. p. uranyl acetate, $UO_2.(C_2H_3O_2)_2.2H_2O$, per liter of solution. This solution is 0.0005 *M* with respect to uranyl acetate, and is generally satisfactory for exposure in bright sunlight up to 6 hours. For exposure of 3 hours or less, the use of a solution 0.001 *M* with respect to uranyl acetate is recommended. The uranyl acetate serves as a sensitizer, causing the decomposition of the oxalic acid in the sunlight. The amount of decomposition is followed by titrating with a standard 0.1 *N* solution of potassium permanganate. The permanganate solution is standardized by titrating the standard oxalic acid–uranyl acetate solution before exposure to sunlight. Exposure of the test solution is carried out in 4 fluid-ounce soft glass oil-sample bottles containing 25 cc. of the solution and stoppered with cotton plugs. The bottles must be carefully cleaned with chromic acid, rinsed with distilled water, and dried. The titrations are made in duplicate. The uranyl acetate used in the standard solution does not affect the titration with permanganate, nor does it cause decomposition of the oxalic acid when stored in the dark without previous exposure to sunlight.

In measuring the sunlight stability of gasoline, a number of bottles containing 25 cc. of the oxalic acid–uranyl acetate solution are placed near the glass pump bowl in such a manner that their exposure to the sunlight is complete. As the test progresses, a bottle is removed at intervals and its contents titrated. When the titration indicates that the pump bowl has had the desired exposure, the color is taken on the gasoline contained therein. The temperature of the gasoline is noted at the beginning and end of the test. The titration with permanganate is carried out in the usual manner. The contents of the actinometer bottle are transferred to a beaker together with washings. Twenty-five cubic centimeters of 2 *N* sulfuric acid are then added and the volume brought to 200 cc. with distilled water, heated to 170° F. (76.67° C.) and titrated to the usual pink end point.

As has been mentioned, it is suggested that a 0.0005 *M* uranyl acetate solution be used for exposures of 3 to 6 hours and a 0.001 *M* solution for exposures of 3 hours or less. In no case should the decomposition be carried beyond 100 mg. of oxalic acid per 25 cc. In Table I is given a comparison between these two solutions.

Table I—Comparison of Uranyl Acetate Solutions of Different Molarity

Duration of Exposure	Oxalic Acid Decomposed: 0.0005 *M* soln.	Oxalic Acid Decomposed: 0.001 *M* soln.	Ratio: 0.001 *M* / 0.0005 *M*
Hours	*Mg.*	*Mg.*	
1½	13.86	23.94	1.727
3	35.28	60.48	1.714
4½	57.96	100.17	1.714
6	74.97	134.19	1.790

Table I shows that exposures made with one concentration are readily convertible to those made with another concentration.

Results

In Table II are given the results of two experiments made at 77° F. (25° C.) on two samples of gasoline of quite different character, in strong and weak sunlight.

Table II—Discoloration of Gasoline in Sunlight of Different Intensity

Strong Light: Time of exposure	Strong Light: Saybolt color	Strong Light: Oxalic acid decomposed	Weak Light: Time of exposure	Weak Light: Saybolt color	Weak Light: Oxalic acid decomposed
Hours		*Mg.*	*Hours*		*Mg.*
STEAM-REFINED MIDCONTINENT GASOLINE					
0	28	0.0	0	28	0.0
2	26½	10.7	2	27½	4.4
6	26	27.1	6	26½	15.1
12	22	64.2	12	26	29.6
18	21	83.1	18	23	50.4
VAPOR-PHASE REFINED CRACKED GASOLINE					
0	25	0.0	0	25	0.0
5	18½	37.0	15	18½	31.5

From these tests it is seen that in one case three times the exposure was required to get the same discoloration in the gasoline in weak as in strong sunlight, and that the oxalic acid decomposed was approximately the same for the same change in gasoline color.

Effect of Temperature

In order to investigate the effect of temperature on the discoloration of gasoline in the sunlight, experiments were made in a special apparatus such that the temperature could be

[1] Received March 17, 1931. Presented before the Division of Petroleum Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Present address, 412 Greenpoint Ave., Brooklyn, N. Y.

controlled. This apparatus consisted of a condenser of soft glass having a spiral inner tube through which water of any desired temperature could be circulated. The gasoline was contained in the outer jacket into which was sealed a thermometer. The gasoline quickly attained and held the temperature of the circulating water. The results of tests on a sample of vapor-phase refined cracked gasoline at three temperatures are given in Table III.

Table III—Effect of Temperature on Discoloration of Gasoline in Sunlight

Temp.	Color after 15 hrs. Exp. to Sunlight[a]	Color after 15 hrs. Exp. to Sunlight and 24 hrs. Storage in Dark	Gum, Steam-Oven Test	Oxalic Acid Decomposed[b] 0.001 *M*	Oxalic Acid Decomposed[b] 0.0005 *M*
° *F.*			*Mg.*	*Mg.*	*Mg.*
53	21	18½	2.3	37	20.7
77	20	18½	5.0	37	20.7
95	19½	18½	3.6	37	20.7

[a] The gasoline prior to exposure had a color of 25.
[b] 15 hours.

From these results it will be observed that for this particular gasoline the effect of temperature on discoloration in the sunlight was not of any great importance. It cannot be assumed, however, that such will be the case for all gasolines. For strictly comparable results, therefore, information relative to the effect of temperature on any gasoline should be obtained before attempting a comparison of sunlight color-stability tests made at different temperatures. The importance of this in comparing tests made in visible pump bowls in the winter and summer is obvious.

Effect of Storage on Gasoline Exposed to Sunlight

Another point of interest in connection with the discoloration of gasoline in the sunlight is that such discoloration when once started continues to get worse during subsequent storage in the dark. In Table III some results indicative of this fact are given, and in Table IV will be found additional data illustrating this point. The three tests were made in sunlight of different intensities.

Table IV—Effect of Exposure to Sunlight Followed by Storage in Dark on Color of Vapor-Phase Refined Gasoline of 25 Colors

Test	Duration	Oxalic Acid Decomposed	Color Immediately after Exp.	Color after Exp. and 24 hrs. Storage in Dark
	Hours	*Mg.*		
1	5	25.2	21	18½
2	5	17.6	22	19
3	5	11.3	24	20

It is recognized that the distribution of spectral energy of sunlight is highly variable, and that for strictly comparable results filters should be used such that only that portion of the light which is completely absorbed by both the actinometer and gasoline is utilized (*1*). The accuracy of reading the color on the Saybolt chromometer, however, is not sufficient to justify such a refinement.

The following precautions should be observed:

The containers for the actinometer solution and for the gasoline should be of the same general character of glass.

The actinometer solution should be titrated immediately after exposure, as the decomposition of the oxalic acid progresses to a slight extent in the dark after having been exposed to the sunlight.

The color should be taken on the gasoline immediately following exposure or at some specified and constant time thereafter, since the discoloration started in the light continues to occur to some degree in the dark.

Tests on the stability of gasoline to sunlight should, when possible, be completed in a single day. When this is not possible or desirable, fresh actinometric solution should be used on the second day and the total exposure be determined by the sum of the amounts of oxalic acid decomposed on the first and second days.

Literature Cited

(1) Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).
(2) Mathews and Dewey, *J. Phys. Chem.*, **17**, 216 (1913).

All-Glass Steam Distillation Apparatus for Analytical Purposes[1]

Victor E. Wellman

The B. F. Goodrich Company, Akron, Ohio

THE necessity of determining precisely small amounts of aniline present in mixtures of various compositions whose other constituents were non-volatile with steam, led to the development of the one-piece all-Pyrex glass apparatus shown in the accompanying diagram.

The steam-distillation flask, *B*, has a steam inlet, *A*, sealed into it a little to one side of the true bottom. Flask *B* is tilted to prevent any froth which may form (as often happens with alkaline solutions) from climbing easily into the Hopkins distillation head, *C*. The delivery tube from *C* is sealed to a safety bulb, *D*, which is placed at the top of the condenser tube, *E*. The sample is introduced into *B* by means of a small-stemmed funnel placed in *A*. In case the material is a solid, it may be dissolved in some low-boiling solvent, such as alcohol, and introduced in solution form, or may be powdered and flushed into *B* with water. Steam is then admitted through *A*, and if necessary the distillation is furnished additional heat from a burner, *G*. The distillate is collected in any suitable receptacle, such as beaker *F*, which may be cooled if necessary.

In the particular work mentioned above the mixture containing aniline was introduced into the flask, after which an excess of sodium hydroxide solution was admitted through *A*. The steam-distilled aniline was collected in a beaker of dilute hydrochloric acid. The entire apparatus was clamped to one ringstand, making it possible to remove the residue quantitatively from the distillation flask by tilting the stand so that the liquid flowed from *A*.

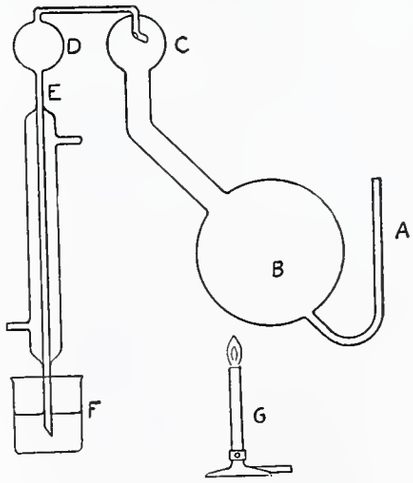


Diagram of Apparatus

The apparatus will be found useful in quantitative work particularly, and generally whenever the distillate is of such nature as to prevent the use of corks, metal foil-covered corks, or rubber stoppers in the neck of the distilling flask.

[1] Received March 13, 1931.

Notes on Use of Glass Color Standards for Determination of Phosphorus by Deniges Colorimetric Method[1,2]

H. D. Chapman

University of California, Riverside, Calif.

An unsatisfactory feature of the blue colorimetric method for the determination of phosphorus is the rapidity with which the color fades necessitating the preparation of new standards frequently. Recently permanent glass color standards to be used in the Hellige comparator for the colorimetric determination of phosphorus by the above method have been placed on the market. A few notes regarding the accuracy of readings made with this equipment and sources of error to be guarded against are presented in this communication.

Experimental Procedure

The color standards, ten in number, are mounted on a circular frame, each one being designated by the Arabic numerals 1, 2, 3, ... 10, and when used in accordance with a given technic supposedly represent phosphorus concentrations increasing uniformly from 0.187 to 1.87 p. p. m. PO_4. The construction of the Hellige comparator and the circular frame is such that upon rotation of the latter the different circular plates are brought into a field in juxtaposition with the unknown. Further information concerning the Hellige comparator and accessories may be found in chemical apparatus catalogs.

Preliminary tests revealed that the color quality of the glass standards matched the actual blue color of phosphorus solutions very well, and that differences in color intensity between succeeding standards were sufficient to permit of several interpolated readings. Inasmuch as the color plates had been standardized by a method different in technic from the one in use in this laboratory, it first of all became necessary to establish values for each by the particular method employed here.

This method is essentially the same as that outlined by Truog and Meyer (*1*). The solution to be tested is combined with 4 cc. of reagent A (2.5 per cent ammonium molybdate in 10 *N* sulfuric acid), made up to a volume of 99.5 cc. with distilled water, and 10 drops (0.5 cc.) of 2.5 per cent stannous chloride reagent added.

Solutions of known phosphate content were prepared and readings taken at exactly 2 minutes following the addition of the stannous chloride. All determinations were made with solutions brought to a temperature of 24.5° C. A daylight lamp to insure uniformity of light, a metal support for the comparator, and dark background to reduce reading strain, all combined to increase the reading accuracy. An attempt was made to interpolate ten degrees of color intensity between each one of the standards; for example, between the color plates 1 and 2, to estimate degrees of color corresponding to values of 1.1, 1.2, 1.3, etc. Three individual determinations were made for each phosphate concentration. The values found are recorded in Table I. By plotting and interpolation the phosphate equivalent for each of the ten color plates was found. These values are given in Table II.

The differences between succeeding color plates are not absolutely uniform. Whether this non-uniformity is due to the color plates themselves or to a lack of proportionality of the color developed from increasing phosphate concentrations cannot be stated. In any case it is not permissible to establish a value for one standard and assume that the values of the other nine are perfect multiples.

Table I—Readings Made with Solutions Containing Varying Concentrations of PO_4

PO_4 Concentration	Readings			
	a	*b*	*c*	Mean
P. p. m.				
0.30	1.3	1.5	1.5	1.43
0.34	1.6	1.6	1.7	1.63
0.38	1.9	2.0	...	1.95
0.43	2.1	2.3	2.4	2.26
0.46	2.4	2.6	2.7	2.56
0.49	2.6	2.7	2.6	2.63
0.52	2.9	2.8	2.8	2.83
0.55	3.1	3.1	2.9	3.03
0.60	3.4	3.5	3.3	3.40
0.64	3.8	...	3.7	3.75
0.69	4.0	3.9	3.8	3.90
0.76	4.5	4.4	4.5	4.46
0.92	5.0	5.1	5.1	5.06
0.99	5.8	5.4	5.5	5.56
1.07	5.9	5.7	5.8	5.80
1.15	6.4	6.0	6.1	6.16
1.22	6.8	6.7	6.8	6.76
1.30	7.1	7.2	7.2	7.16
1.38	7.3	7.5	7.6	7.46
1.45	7.7	7.7	7.7	7.70
1.53	7.8	8.1	8.0	7.96
1.61	8.9	8.3	8.5	8.56
1.68	9.1	8.8	8.8	8.90
1.76	9.3	9.3	9.3	9.30
1.83	...	9.5	9.4	9.45
1.91	...	9.7	9.7	9.70

Table II—Phosphate Equivalent of Color Standards

Color Standard	PO_4 Equivalent	Difference between Successive Standards
	P. p. m.	
1	0.235	...
2	0.385	0.150
3	0.535	0.150
4	0.690	0.155
5	0.875	0.185
6	1.080	0.205
7	1.285	0.205
8	1.490	0.205
9	1.695	0.205
10	2.020	0.325

The data of Table I give considerable information as to the agreement possible between repeated independent readings on solutions of the same phosphate concentrations. In general the differences between repeated observations are practically the same with both high and low phosphate concentrations, and there appears to be no particular range where readings are more accurate. It is apparent that the use of these standards permit of sufficient accuracy for most purposes.

Precautions to Observe

Use of Stannous Chloride—In the course of studies in connection with the blue colorimetric method, it has been found that stannous chloride solutions stored in bottles and protected from the air by a layer of mineral oil, as suggested by Truog and Meyer (*1*), will nevertheless gradually deteriorate. At the end of 10 months a 2.5 per cent solution was found to have become about 80 per cent oxidized.

[1] Received March 27, 1931.

[2] Paper No. 248, University of California, Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, Calif.

Oxygen is appreciably soluble in paraffin oil, and it is therefore obvious that protective layers of this liquid can be only partially effective in preventing the diffusion of the oxygen of the air into the stannous chloride. Unless prepared fresh or stored under conditions known to preclude oxidation, this reagent should be checked occasionally in order that the same quantities can be added to unknowns as were used in the standardization of the permanent standards. Minor variations in the quantities of stannous chloride added produce no important effect upon the color intensity developed. The use of solutions which have become as much as 80 per cent oxidized, however, will introduce serious errors. When freshly prepared solution standards are used in place of permanent standards, this deterioration is obviously not serious, for both standard and unknown are affected similarly.

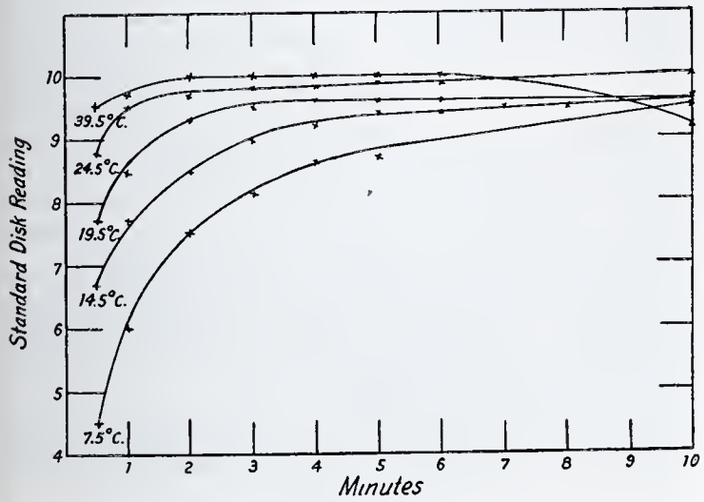


Figure 1—Effect of Temperature on Rate of Development of Blue Color

Preliminary experiments under way to compare various methods of storing stannous chloride indicate that protection by alkaline pyrogallate is more effective than protection by oil layers.

Effect of Temperature—It has frequently been observed that with cool solutions the reduction reaction apparently does not proceed as rapidly as when the solutions are warm. Temperatures in this laboratory vary at times from 15° to 35° C. If temperature materially affects the rate at which the color intensifies, it is possible that a reading at 15° C., taken 1 or 2 minutes following the addition of stannous chloride, might be considerably different from a reading made at 35° C., following the same technic.

To secure quantitative information on the relative importance of this temperature factor, test solutions of known phosphate concentration were prepared, brought to a given temperature, and after the addition of reducing agent compared at intervals with the glass standards. The solutions were held at the temperature specified during the entire period of observation. The data secured on the rate of development of color at varying temperatures for each of several different phosphate concentrations are recorded in Table III.

In general the results for the different phosphate concentrations used are of the same type. A portion of the data obtained with solutions containing 1.91 p. p. m. PO_4 are shown graphically in Figure 1.

It is clear that there is a measurable time factor in the rate at which the reduction reaction proceeds. Readings made after a given interval at one temperature may be considerably different from the values obtained at a different temperature. The magnitude of this difference decreases with increasing time intervals; in other words, there is an evident tendency for the same maximum value to be obtained regardless of temperature. However, the data are not complete enough to establish this point definitely, and certain considerations indicate that this may not necessarily be the case. It will be noted that after an interval of 10 minutes some of the solutions had begun to fade. This fading is probably due to oxidation of the blue compound by the oxygen of the air, and apparently begins after a part or all of the excess stannous chloride added is oxidized. If, as appears entirely tenable, the rates of the reduction and oxidation reactions are not affected exactly the same by temperature differences, then the total colors produced by a given phosphate concentration need not necessarily be the same where the temperatures of the solutions differ.

A disturbing color tint which develops a few minutes after

Table III—Effect of Temperature upon Rate of Color Development

PO_4 Concn.	Temp.	Readings at Various Minute Intervals after Addition of Stannous Chloride																
		1/2	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	25
	° C.																	
1.91	7.5	4.5	6.0	7.5	8.1	8.6	8.7	...	...	...	...	9.5	...	...	...	...	...	9.5
	14.5	6.7	7.7	8.5	9.0	9.2	9.4	9.4	9.5	9.5	9.6	9.6	9.6	9.6	9.7	9.7	9.7	9.5
	19.5	7.7	8.5	9.3	9.5	9.6	9.6[a]	9.6[a]	...	...	...	9.6[a]	...	...	...	...	...	...
	24.5	8.8	9.5	9.7	9.8[a]	9.8[a]	9.9[a]	9.9[a]	...	...	...	10.0[a]	...	...	...	...	...	...
	29.5	8.8	9.5	9.7	9.7[a]	10.0[a]	10.0[a]	10.0[a]	...	...	...	9.7[a]	...	...	...	...	...	...
	34.5	9.2	9.5	9.7	10.0[a]	10.0[a]	10.0[a]	10.0[a]	...	...	...	9.5[a]	...	...	...	...	...	...
	39.5	9.5	9.7[a]	10.0[a]	10.0[a]	10.0[a]	10.0[a]	10.0[a]	...	...	...	9.2[a]	...	...	...	...	...	...
1.53	14.5	5.3	6.7	7.2	7.4	7.6	7.7	7.8	7.8	7.8	7.8	7.8*	7.8	7.8	7.9	7.9	7.9	...
	19.5	6.0	7.0	7.5	7.6	8.0[a]	8.0[a]	8.0[a]	...	...	...	8.0[a]	...	...	...	...	...	...
	24.5	7.4	7.6	7.9	8.1[a]	8.3[a]	8.4[a]	8.4[a]	...	...	...	8.4[a]	...	...	...	...	...	...
	29.5	7.4	7.8	8.1	8.2[a]	8.4[a]	8.4[a]	8.4[a]	...	...	...	8.4[a]	...	...	...	...	...	...
	34.5	7.5	7.8	8.0	8.2[a]	8.3[a]	8.3[a]	8.3[a]	...	...	...	7.5	...	...	...	...	...	...
	39.5	7.6	7.7	8.0	8.0[a]	8.1[a]	8.1[a]	8.1[a]	...	...	...	...	...	...	...	...	...	...
1.15	14.5	4.3	4.8	5.3	5.7	6.0[a]	6.1[a]	6.2[a]	6.3[a]	6.5[a]	6.5[a]	6.5[a]	6.6[a]	6.6[a]	6.6[a]	6.6[a]	6.6[a]	...
	19.5	4.5	5.3	5.8	5.9	6.1[a]	6.5[a]	6.6[a]	...	...	...	6.6[a]	...	...	...	...	...	...
	24.5	5.7	6.0	6.6[a]	6.7[a]	6.8[a]	6.8[a]	6.8[a]	...	...	...	6.8[a]	...	...	...	...	...	...
	29.5	5.6	6.0	6.5[a]	6.6[a]	6.7[a]	6.7[a]	6.8[a]	...	...	...	6.7[a]	...	...	...	...	...	...
	34.5	5.8	6.4	6.5	6.6[a]	6.6[a]	6.6[a]	6.5[a]	...	...	...	6.5[a]	...	...	...	...	...	...
	39.5	5.8	6.4[a]	6.4[a]	6.5[a]	...	...	...	...	...	...	...	...	...	...	...	...	...
0.76	14.5	2.8	3.3	3.9	4.2	4.2	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.3	4.4	4.4	4.4	...
	19.5	3.0	3.6	3.9	4.1	4.4[a]	4.4[a]	4.4[a]	...	...	...	4.4[a]	...	...	...	...	...	...
	24.5	3.9	4.1	4.4	4.4[a]	4.6[a]	4.7[a]	4.8[a]	...	...	...	4.6[a]	...	...	...	...	...	...
	29.5	4.2	4.4	4.4	4.5[a]	4.5[a]	4.6[a]	4.6[a]	...	...	...	4.5[a]	...	...	...	...	...	...
	34.5	4.3	4.3	4.4[a]	4.5[a]	4.5[a]	4.5[a]	4.5[a]	...	...	...	4.5[a]	...	...	...	...	...	...
0.38	14.5	1.2	1.5	1.7	1.8	1.9	1.9	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	...
	19.5	1.4	1.6	2.0	2.1[a]	2.1[a]	2.1[a]	2.1[a]	...	...	...	2.1[a]	...	...	...	...	...	...
	24.5	1.8	2.0	2.2	2.3[a]	2.4[a]	2.4[a]	2.4[a]	...	...	...	...	...	...	...	...	...	...
	29.5	1.9	2.0	2.0	2.1[a]	2.1[a]	2.2[a]	2.3[a]	...	...	...	2.3[a]	...	...	...	...	...	...
	34.5	1.9	2.0	2.0	2.1[a]	2.2[a]	2.2[a]	2.3[a]	...	...	...	2.2[a]	...	...	...	...	...	...

[a] Color tint of unknown and standard different.

the addition of stannous chloride is due to the action of this reagent on ammonium molybdate itself. This fact, together with the above doubt as to the final development of the same color intensity at different temperatures from a given phosphate concentration, points to the desirability, though possibly not absolute necessity, of making readings at 1 or 2 minutes following the addition of reducing agent. If this practice be adopted, the elimination of errors arising from temperature differences can be effected by any one of several alternative procedures. The glass color plates can be standardized by a given technic at various temperatures, or having established values for them at one temperature, all solutions to be tested can be brought to the same temperature before the addition of the reducing agent; or, finally, having standardized the color plates at one temperature, allow sufficient time to elapse with unknowns of different temperatures to permit the color to intensify to the same point as in the standard.

Conclusions

The use of permanent glass color standards offers a means of eliminating one of the unsatisfactory features of the blue molybdate method for the colorimetric determination of phosphorus. The color of these glass standards matches the color of the reduced phosphate solutions very well. A degree of accuracy sufficient for practical purposes can be attained if certain details pertaining to the technic of the determination are followed.

It is first of all necessary to establish values for each of the ten circular color plates, for they do not vary uniformly in color.

Stannous chloride solutions, although protected from the air by layers of mineral oil, will nevertheless gradually become oxidized. Since it is essential that approximately the same quantities of this reagent be used in the tests as were used in the standardization of the color plates, the strength of this solution should be checked now and then unless it is stored under conditions known to preclude oxidation.

It has been found that the rate of the reduction reaction is measurably affected by such changes in temperature as may occur in some laboratories. Unless laboratory temperatures are uniform, some one of the alternative procedures suggested in the text should be adopted in order to eliminate possible errors arising from this source. When freshly prepared solution standards are used in place of permanent standards, neither the deterioration of stannous chloride nor temperature differences are serious considerations, since these influences are obviously operative on both standard and unknown.

At the present time nothing can be stated regarding the permanency of these glass standards. In order to guard against the possible gradual fading which may conceivably take place, it is suggested that the values found for each color standard be checked occasionally.

The use of permanent standards makes it possible to save considerable time in the routine determination of phosphorus with but little sacrifice in accuracy.

Literature Cited

(1) Truog and Meyer, Ind. Eng. Chem., Anal. Ed., 1, 136–9 (1929).

Analysis of Gaseous Hydrocarbons

A Short-Cut Method[1]

R. Rosen and A. E. Robertson

Standard Oil Development Co., P. O. Box 485, Elizabeth, N. J.

As a result of the study of a number of synthetic mixtures of gaseous hydrocarbons, a master graph is presented whereby from an ordinary distillation analogous to an Engler distillation of petroleum products, the analysis of certain gaseous hydrocarbon mixtures may be obtained.

A simplified apparatus and procedure are described for the analysis of gaseous mixtures by the proposed short-cut method.

A section of the master graph is given in detail, the range being that corresponding to the composition of certain refinery gases. The application of the short-cut method to the analysis of these gases is discussed.

Since the refinery gases considered contain unsaturates and isomers as well as the corresponding normal saturated hydrocarbons, a study was made of their effect upon the nature of the distillation curve, and a correction curve for this effect is presented.

Analysis of gases may be completed in 60 to 75 minutes, and only 200 to 250 cc. of liquid nitrogen are required for an analysis. The technic of analysis is easily acquired.

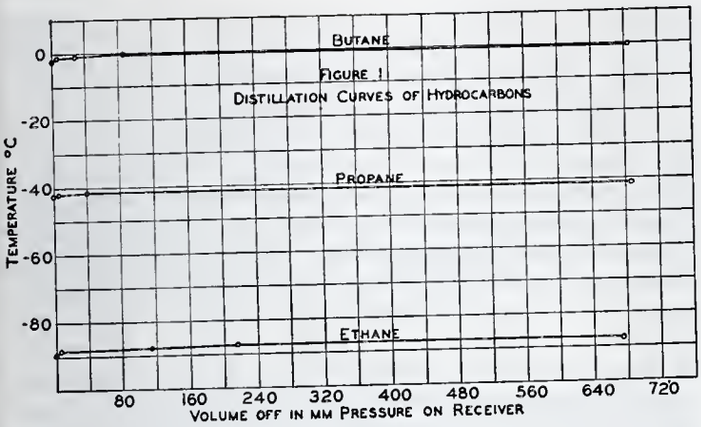
Because of its economical features, the short-cut method proposed offers considerable promise as a routine method of control analysis for the operation of various equipment, once the master graphs, or detailed graphs covering the range desired, are prepared.

With the increasing importance of the lighter hydrocarbons either as gases or as constituents in petroleum products, the necessity for rapid and accurate methods for their analysis into their individual constituents is generally recognized. The use of fractionation equipment such as the Podbielniak apparatus (*2*, *3*) for the analysis of gaseous mixtures is quite prevalent in the oil industry. This method at best requires a skilful operator, consumes 2 to 5 liters of liquid air or nitrogen, and requires 3 to 8 hours for a complete analysis. Furthermore, large volumes of gas must be used for the analysis of samples containing only small percentages of one component—e. g., dry gases (*4*). In view of this situation, a simple and rapid method of hydrocarbon analysis, which would consume little or no liquid air or nitrogen, would find considerable application in the industry for routine control purposes.

The object of this work was to develop such a method embodying the features enumerated.

Hydrocarbon analysis by present methods involves fractional distillation in a suitable microfractionating column. The fractionation is conducted preferably at atmospheric pressure and the individual hydrocarbons are taken overhead at their corresponding boiling points. The percentages of the hydrocarbons are determined directly from the fractional-distillation curve plotted for the temperature of the

[1] Received March 17, 1931. Presented before the Division of Petroleum Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.



overhead vapor against the amount of distillate. In contrast to this, the method proposed here involves ordinary distillation of the condensed gaseous mixture at atmospheric pressure, in a manner analogous to an Engler distillation of petroleum products. A method applying this principle and applicable to the analysis of mixtures of benzene, toluene, and xylene was described by Colman and Yeoman (*1*). A similar method applicable to the analysis of natural gasoline was reported by Smith (*5*).

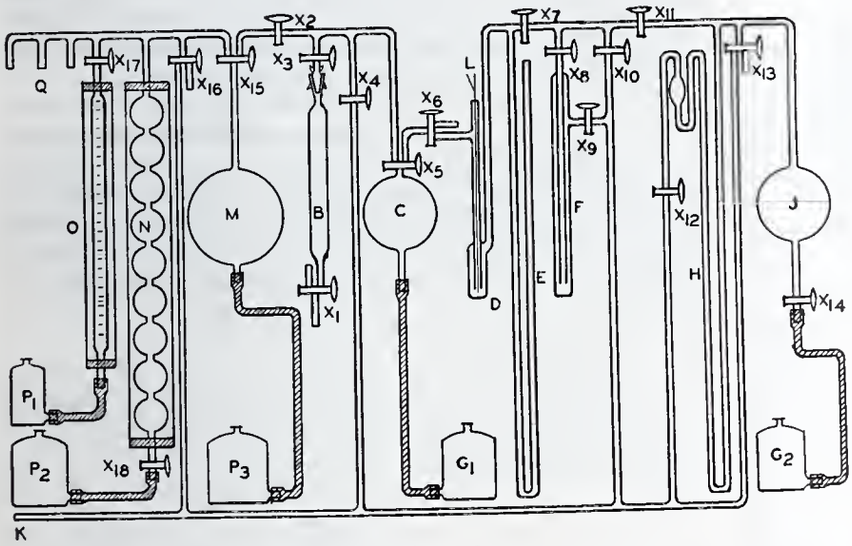


Figure 2

The first part of the paper presents a proposed short-cut method developed on the basis of synthetic mixtures of pure saturated hydrocarbons. It gives the first of a series of graphs whereby, from an ordinary distillation, the analysis of ternary mixtures of the hydrocarbons ethane, propane, and butane over a limited range may be obtained. The second part of the paper shows the application of this method and the use of the graph for the analysis of refinery gases. It also discusses the effect of unsaturated hydrocarbons and isobutane when they are present in addition to the normal saturated hydrocarbons considered.

Description of Method

The method of analysis proposed is limited in its present form to the analysis of three component mixtures, although four components may be determined if one is methane or "fixed gases,"—i. e., gases that do not condense at the temperature of boiling nitrogen, as carbon monoxide, hydrogen, nitrogen, and oxygen.

In the development of the method, synthetic ternary mixtures of the pure hydrocarbons ethane, propane, and butane, covering a considerable range of composition, were made up. These gaseous mixtures were condensed and distilled by the procedure given. Distillation curves representing temperature against percentage by volume distilled off were obtained in this manner. From these curves, the temperatures at two chosen percentages off were taken and plotted against each other on ordinary graph paper. Lines were drawn through all points having the same concentration of one component and another set of lines drawn through all points having the same concentration of another component. A graph showing these two sets of lines is sufficient to define any composition of the ternary mixture for the range covered.

Since it was impractical to prepare a detailed graph covering the entire range of composition for the ternary mixture ethane, propane, and butane, sufficient data were obtained to prepare a skeleton graph covering the entire range. In addition, however, a section of this graph that covers the range of certain gases encountered in refinery practice was prepared in detail.

Raw Materials—The hydrocarbons ethane, ethylene, propane, propylene, butane, and isobutane, used in the preparation of all synthetic mixtures throughout the work, were available in 3-pound (1.36-kg.) steel cylinders. Analysis of these gases by an improved microfractionating column showed that from 1 to 2 per cent of fixed gas was present. This was removed by cooling the cylinders by means of liquid nitrogen to temperatures at which the vapor pressure of the hydrocarbon is less than 1 mm., and then pumping the cylinders with a high-vacuum pump for an hour. In this manner the percentage of fixed gas was reduced to about 0.2 per cent and correction for this residual gas was made in preparing the synthetic mixtures.

The hydrocarbons were then distilled by an apparatus described in this paper to give the distillation curves plotted in Figure 1. These curves show that practically the entire volume of each gas is distilled off at a constant temperature. Since it has been shown by Washburn (*6*) that constancy of pressure during isothermal vaporization is an excellent criterion for purity, it is evident from Figure 1 that the hydrocarbons used in this work possessed a high degree of purity.

Description of Apparatus—The apparatus used in the preparation of the synthetic mixtures and in their distillation is shown in Figure 2.

The portion to the left represents the equipment used in the preparation of synthetic mixtures. It consists of the 100-cc. water-jacketed buret, O, graduated in tenths of a cubic centimeter and equipped with the leveling bulb P_1. The water-jacketed buret, N, of 900 cc. capacity is graduated in 100 cc. P_2 is the leveling bulb for N. The reservoir of 1000 cc. capacity for storing synthetic samples, M, is equipped with leveling bulb P_3. The three connections at Q designate the lines leading to the steel cylinders containing the pure hydrocarbons.

The portion of the figure to the right represents the equipment used in making the distillations of the synthetic mixtures. It consists of tube D in which the gas is condensed and subsequently distilled, and X_1 to X_{18} are various stop-

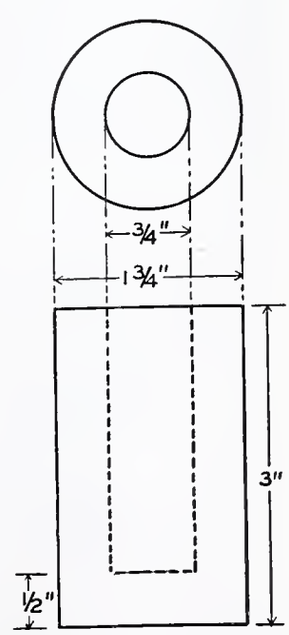


Figure 3

cocks used as indicated. Tube D is equipped with a thermocouple which rests on the bottom of the tube. Thermocouple leads, L, are sealed to this tube by means of deKhotinsky cement. The thermocouple is single junction and is made of No. 36 copper and constantan wires. The temperature is indicated by means of a precision potentiometer, although one reading to tenths of a millivolt may be used if a triple-junction thermocouple is substituted for the single junction. Crushed ice in a thermos bottle is used for the cold junction.

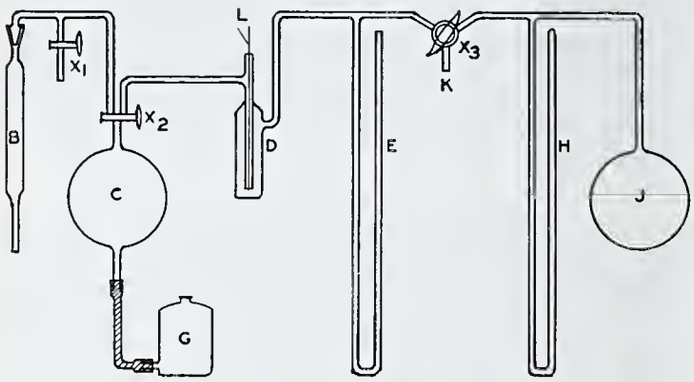


Figure 4

The fixed gas and methane are pumped off through a trap, F, while the sample is surrounded by liquid air. The sample, if not synthetic, is introduced through B, a drying tube filled with Desicchlora (anhydrous barium perchlorate). C is a calibrated flask for measuring the volume of the sample introduced, and J is a calibrated expansion bulb for collecting the gas during the distillation. H is a closed-end manometer equipped with a mercury seal, for indicating the pressure in the bulb J, and E is an open-end manometer to measure the pressure in the distillation tube D. G_1 is a leveling bulb for bulb C. G_2 is a leveling bulb for expansion bulb J, and is provided so that, if desired, the sample may be removed from the apparatus by mercury displacement for further examination, after the distillation is finished. In such a case, the sample would be removed through stopcock X_{13}.

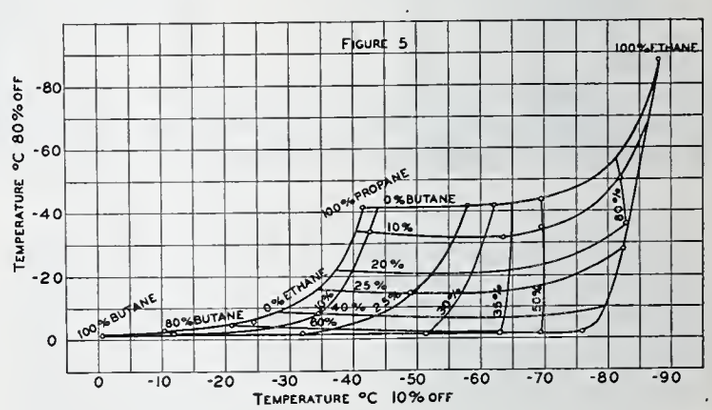
Procedure for Making Synthetic Mixture—Prior to making up a synthetic mixture, the burets O and N and storage bulb M (Figure 2) are filled with mercury, and the lines from X_2 to Q are evacuated. A gas is now released from its cylinder into the burets O and N displacing the mercury therein. The mercury levels are adjusted to the desired marks by manipulating the proper leveling bulbs, making sure that the gas is under slight pressure. The excess pressure is vented to the atmosphere through stopcock X_{16}. The gas is now transferred to bulb M, care being taken that the lines are left at atmosphere pressure. The lines are evacuated before introducing another gas. In this manner, each of the gases is introduced in the volume required to make up the synthetic mixture desired.

Procedure for Analysis—The apparatus from X_3 to J (Figure 2) is evacuated. With stopcock X_4 closed, the sample is transferred from storage bulb M, or from outside container through stopcock X_1, to the flask C. The sample is held under slight pressure while the level is adjusted to the mark with leveling bulb G_1. Excess pressure is released by opening stopcock X_5 to X_6 to the atmosphere. Stopcock X_6 is closed, and tubes D and F are surrounded with Dewar flasks containing liquid nitrogen or air. Stopcocks X_7 to X_{11} are closed, while stopcock X_6 is opened to tube D and the sample is allowed to condense in the tube.

If pressure shows on the manometer, E, the presence of fixed gas or methane is indicated since the vapor pressure of ethane is only 0.1 mm. mercury at the boiling point of nitrogen. The fixed gas is readily removed by pumping with the mercury vapor pump, K, upon opening stopcocks X_7 to X_9. When methane is present, it is necessary to remove it from solution. This is accomplished by warming tube D until the vapor pressure of the liquid reaches atmospheric pressure, cooling the tube with liquid nitrogen to recondense the sample, and pumping off the released methane. This process is repeated until the removal of all the methane is assured—i. e., until no pressure is indicated on the manometer at the temperature of boiling nitrogen. When this has been completed, the stopcock X_9 is closed, stopcocks X_7 and X_8 are opened, and the liquid nitrogen removed from tube F. Tube F is warmed to room temperature. If ethane should condense in F, it is distilled back into tube D after which stopcock X_8 is closed. During the removal of fixed gas and methane, trap F is used to prevent any ethane and heavier hydrocarbons from being pumped off.

An aluminum cylinder (Figure 3) bored to fit snugly around tube D is cooled by immersion in liquid nitrogen to a temperature below the boiling point of the mixture to be examined and placed around tube D. The cylinder is surrounded by a Dewar flask and covered with cotton felt at the top to insure uniform heating of the still. Heat input to the cylinder, and hence to the still, is controlled by lowering the Dewar flask and thus increasing the surface of the cylinder which is exposed to room temperature.

The distillation is conducted at atmospheric pressure by cracking stopcock X_7 as the pressure tends to exceed atmospheric. The distillate is collected as a gas in the previously evacuated calibrated expansion bulb. The temperature of the liquid being distilled is given by the thermocouple, which is made of very fine wire to prevent conduction of heat, a precision potentiometer being used for reading the temperature.



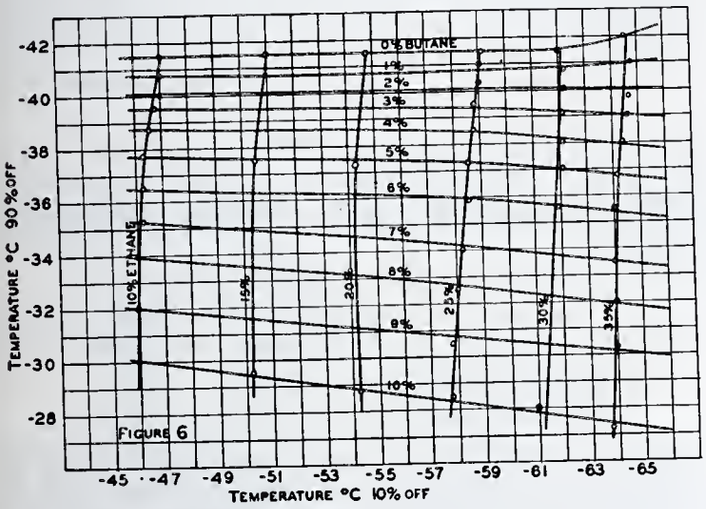
In order that the results may be comparable, distillations are conducted at 760 mm. instead of atmospheric pressure. This is accomplished by regulating stopcock X_7 so that the pressure observed on manometer E is always 760 mm. This regulation is acquired with practice. It is necessary to hold the pressure constant to within a few millimeters in order to obtain check results. The distillation should be conducted at a fairly constant rate of an average of about 15 cc. of gas per minute. During the distillation, simultaneous readings on the potentiometer and the manometer H are taken, as the voltage changes 0.1 or 0.2 millivolt, or as the pressure rises 5 to 10 mm. The distillation is continued while readings are taken.

When the distillation is completed, stopcock X_7 is opened wide and the total pressure, P_2, on the manometer H is noted. From the barometric pressure, the volumes of the measuring flask, still, and expansion bulb, the pressure, P_1, correspond-

ing to the volume of the sample taken is calculated by the formula

$$P_1 = \frac{\text{volume measured} \times \text{atmospheric pressure}}{\text{volume of distillation bulb} + \text{lines} + \text{expansion bulb}}$$

The difference between P_1 and P_2 represents the pressure due to fixed gases and methane which are pumped off before the distillation is begun. Its fraction of the total pressure, P_1, gives the percentage of fixed gases and methane in the sample.



A graph is now prepared by plotting the temperature against the pressure in millimeters. From this curve, the temperature corresponding to any percentage off may be read.

Figure 4 is a simplified apparatus recommended for routine analysis of any gaseous mixture by this method. It is similar to the distillation apparatus shown in Figure 2 except that the trap F shown there has been eliminated, since it appears that no appreciable amount of ethane is condensed in it during the removal of fixed gases and methane.

The volumes of those parts of the apparatus shown in Figure 4 which affect the nature of the curves obtained upon distillation are as follows:

Bulb C = 520 cc.
Bulb D + lines from X_2 to X_3 = 14.6 cc.
Bulb J + line from X_3 = 557 cc.

Results—A considerable number of synthetic mixtures of the hydrocarbons ethane, propane, and butane were made up and distilled by the method described. From these distillations, the graphs shown in Figures 5 and 6 were prepared.

Figure 5 is an outline of the master graph showing all possible compositions of the three hydrocarbons. In its present form, it is not intended for use for analytical purposes by the method described, but merely to indicate the general nature of these curves.

Figure 6 gives a section of Figure 5 in detail. It is the first of a series of such sections which it is planned to present. This particular section covers the composition of certain refinery gases and is discussed in the second section of this paper.

Several typical distillation curves are shown in Figure 7. The reproducibility of results is shown in Figure 8, which gives check distillation curves for the same sample. It is to be noted that the two curves are represented by different ordinates so that if superimposed, the curves would almost coincide.

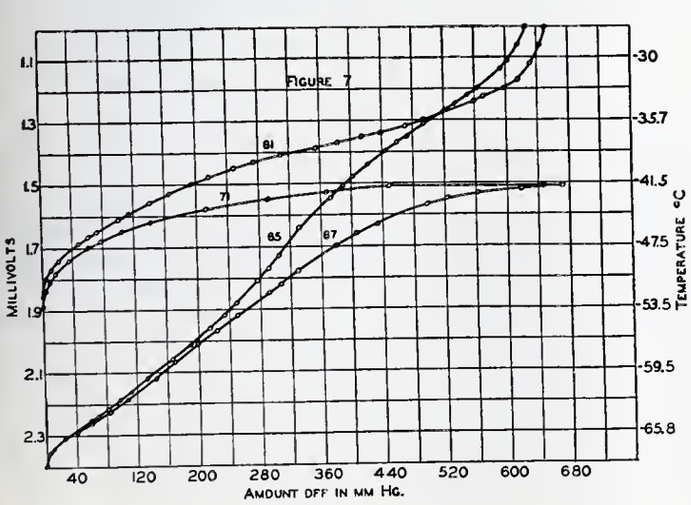
An analysis may be completed in 60 to 75 minutes as compared to 3 to 8 hours by the fractionation methods. The consumption of liquid nitrogen or air is about 200 to 250 cc., most of which is used in cooling the aluminum cylinder. This compares favorably with ordinary fractionation methods which usually require 1000 to 5000 cc.

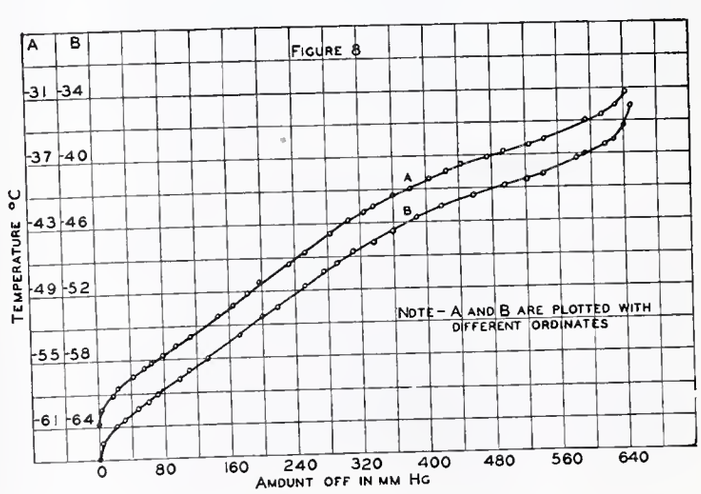
Discussion—It is apparent from Figure 6 that, for the synthetic samples prepared and distilled in the manner described, an excellent regularity is obtained. By the preparation of the necessary synthetic mixtures, the range may be extended in any direction desired, and the same regularity may be expected to prevail over the entire range for the three hydrocarbons considered.

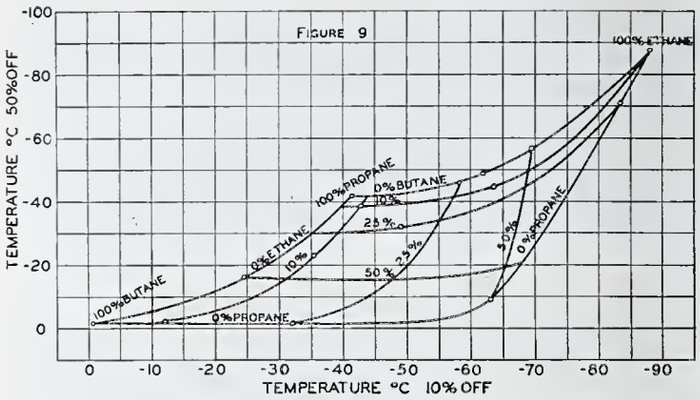
Graphs of a similar nature may be developed for ternary mixtures of other hydrocarbons in a similar manner. In each case, two of the hydrocarbons are obtained by the graph and the third by difference.

Although in Figure 5, the temperatures at 10 per cent and 80 per cent off were chosen, and in Figure 6, the temperatures of 10 per cent and 90 per cent off were used, it is obvious that, for any similar charts which may be prepared, the percentages off that should be chosen are those which will yield satisfactory curves for the range under consideration. For the master graph, it is also obvious that in order to obtain sufficient spread between the curves for the various compositions possible, it is more satisfactory to prepare two or more charts representing temperatures at different percentages off. This is illustrated by Figure 9, where the master graph shown in Figure 5 is drawn for temperatures at 10 per cent and 50 per cent off. This gives a larger spread for the high butane percentages.

The accuracy of the method is governed by the accuracy of the graph, which in turn is dependent upon the reliability of the temperature and pressure readings. A difference of one in the percentage of any of the constituents within the range investigated has a distinct effect on the distillation

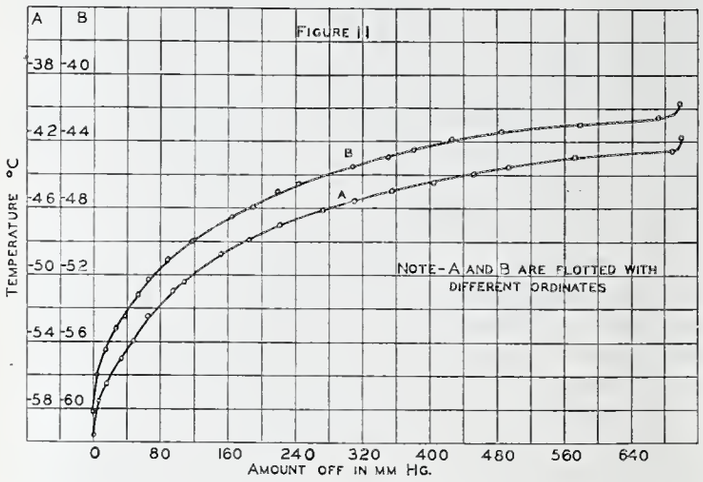






curve, and hence its position within the graph. This is illustrated by Figure 10 which shows the effect of a change of 1 per cent on the butane content of two synthetic mixtures of otherwise similar composition.

Using the apparatus described and operating with the procedure given, it has been shown that check runs on the same sample agree to within 0.5 per cent on any constituent. It follows that the analysis of any ternary mixture of the hydrocarbons included within the range of the graph is reliable to 0.5 per cent. Inasmuch as recent unpublished studies of various equipment for analysis of synthetic gaseous hydrocarbon mixtures show that the maximum accuracy obtainable by the most satisfactory apparatus is not better than an average of 0.5 per cent on each of the constituents present, the results obtained by the proposed method compare favorably with the other equipment.



For ternary mixtures that do not contain any fixed gas or methane besides the three hydrocarbons that make up the mixture, carbon dioxide snow may be used instead of liquid nitrogen or air. As illustrative of the satisfactory use of carbon dioxide for samples of this type, Figure 11 shows two consecutive runs on the same sample, curve *A* obtained when liquid nitrogen was used, and curve *B* when carbon dioxide-acetone slush was used.

Application of Short-Cut Method

In the study and control of various petroleum processes, a knowledge of the composition of gases involved is most important and a method of analysis suitable for routine purposes is desirable. For example, recently a number of refineries have adopted stabilization equipment, the operation of which may be controlled from the analysis of the overhead gas from the stabilizer or of the stabilizer reflux.

Since fractionation of stabilizer gas and stabilizer reflux by a Podbielniak apparatus gave the average analysis shown in Table I, it was the object of this investigation to develop the method that has been described with the view of applying it to analyses of gases of this type. It is for this reason that the detailed graph shown in Figure 6 was prepared.

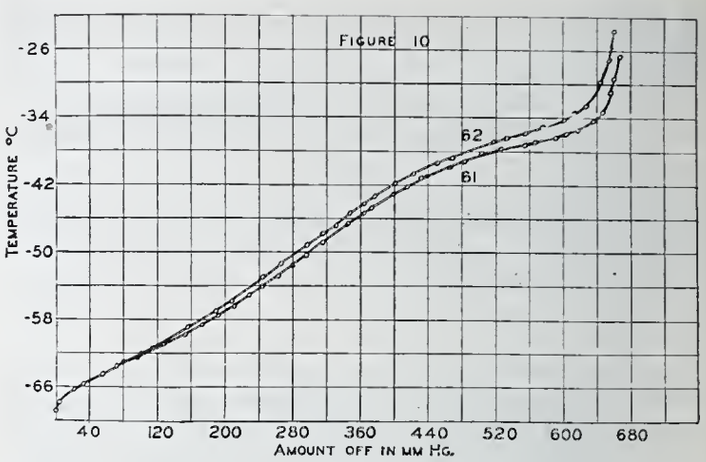
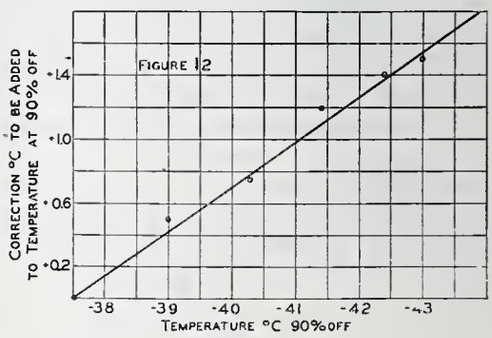


Table I—Analysis by Podbielniak Apparatus

Constituent	Stabilizer Gas	Stabilizer Reflux
	% by vol.	*% by vol.*
Fixed gas and methane	8.0	0.0
Ethane, ethylene	25.0	14.0
Propane, propylene	65.0	82.0
Isobutane, butane	2.0	4.0

After the graph was completed, comparative analysis of stabilizer gas or stabilizer reflux samples by the short-cut method and a Podbielniak column revealed that the short-cut method gave results that were too low, particularly on the butane content. In an attempt to explain this discrepancy, Orsat analyses were made of the individual cuts obtained during the fractionation of average stabilizer gas, and these showed that about 15 per cent of the ethane fraction consisted of ethylene and about 25 per cent of the propane fraction was propylene. Further, fractionation analysis showed that 60 to 80 per cent of the butane fraction was isobutane. Consequently, a study was made of the effect of each of these hydrocarbons, in the concentration given, on the distillation curves of the otherwise similar ternary mixtures described in the first part of the paper. Since for control purposes the butane content of these gases is of primary importance, and, further, since the 90 per cent off-point practically determines the percentage of butane, only the effect upon the 90 per cent point was considered.



Ethylene was found to have no effect on the 90 per cent point even if substituted entirely for ethane. Propylene, on the other hand, affected the 90 per cent point when substituted for propane to the extent of 25 per cent of the total propane fraction. The results of several runs on synthetic mixtures using different concentrations of butane are shown in Figure 12. This curve may be used to correct for propylene if its concentration is of the order given above. For instance if the unknown sample shows a temperature of 42° C. at 90 per cent off, an examination of Figure 12 gives a correc-

tion of +1.3° C. This would be added to −42° C., making −40.7° C. the corrected 90 per cent point. This value would then be plotted against the 10 per cent point, using the graph shown in Figure 6.

Isobutane, in concentration up to 50 per cent of the butane fraction, was found to have no appreciable effect on the 90 per cent point over the range covered by Figure 6.

Applying the above correction for the propylene content, several typical analyses of stabilizer gases and stabilizer reflux are presented in Table II for comparison with the results by the fractionation method.

Since the results of this investigation have been satisfactory for the range covered, it is planned to extend the work with the view of developing graphs which will cover many types of refinery gases.

Table II—Comparison of Short-Cut Method with Fractionation in Podbielniak Column

Constituent	Run 1 Pod.	Run 1 Short cut	Run 2 Pod.	Run 2 Short cut	Run 3 Pod.	Run 3 Short cut
	%	%	%	%	%	%
Fixed gas and methane	9.4	9.1	13.6	12.8	1.6	0.1
Ethane	23.8	23.8	21.1	21.6	13.5	13.2
Propane	63.5	64.1	62.0	62.5	84.2	85.7
Butane	3.3	3.0	3.3	3.1	0.7	1.0

Literature Cited

(1) Colman and Yeoman, *J. Soc. Chem. Ind.*, **38**, 57T (1919).
(2) Podbielniak, *Oil and Gas J.*, **27**, No. 35, 38 (1929).
(3) Podbielniak, *Ibid.*, **28**, No. 20, 235 (1930).
(4) Podbielniak, *Ibid.*, **27**, No. 52, 30 (1929).
(5) Smith, *Ibid.*, **28**, No. 4, 38 (1930).
(6) Washburn, *Z. physik. Chem.*, **130**, 592–600 (1927); Ind. Eng. Chem., **22**, 985–8 (1930).

Apparatus for Experimental Pyrolytic Production of Diphenyl[1]

A. W. Hixson, L. T. Work, H. V. Alessandroni, G. E. Clifford, and G. A. Wilkens

Department of Chemical Engineering, Columbia University, New York, N. Y.

An apparatus is described for the pyrolytic production of diphenyl from benzene, using a bath of molten lead. Trends of conversion efficiency, chemical efficiency, and rate of production are given for various sets of operating conditions with this apparatus. Pressures above atmospheric favor the conversion to diphenyl. The optimum temperature for the reaction is around 740° C.

It has been known for some time that diphenyl could be produced by the pyrolytic decomposition of benzene. Among the early workers in this field were Berthelot (*1*), Schmidt (*7*), and others (*4, 5, 6, 9*) who discovered that diphenyl could be prepared by passing benzene through a red-hot tube. There has been at Columbia University a continuing interest in this pyrolytic action since the first work here by Zanetti and Egloff (*10*). This background, and the recent commercial production of diphenyl, led the authors to seek an apparatus in which diphenyl could be produced continuously without the impedance to flow and the excessively high furnace temperatures which result when tar is deposited. The advantages of a constantly clean surface and of uniform heating possessed by a molten bath seemed desirable here (*2, 3, 8*). In the experiments reported in this paper, lead was used exclusively as the molten bath. The experiments were restricted to benzene, but the apparatus showed possibilities for use in the pyrolysis of other organic substances—for example, toluene, xylene, cymene—and also for the simultaneous interaction of these materials with gases such as chlorine, ammonia, sulfur dioxide, and hydrogen, using suitable baths.

Description and Operation of Apparatus

The apparatus used by the authors is shown in Figures 1 and 2. Referring to Figure 1, *A* is the benzene reservoir; *B*, the preheating vaporizer; *C*, the reactor; *D*, the condensing system; and *E*, the gas meter. The liquid benzene contained in the reservoir *A*, which consists of a standard 3-inch pipe (7.6-cm.) fitted with caps and a graduated sight glass, is passed under pressure maintained by carbon dioxide from a cylinder, through the line *L* to the preheating vaporizer, *B*. The vaporizer is heated by a 12 × 1¼ inch (30.48 × 4.17 cm.) electric resistance furnace. The hot benzene vapors continue up the line *L* and down the central downtake pipe which is surrounded by molten lead to a depth of 17 inches (43.18 cm.) contained in the reactor, *C*. The reactor consists of a ¾-inch (2.5-cm.) extra-heavy seamless steel tube fitted with heavy ammonia flanges and heated by a standard three-section electric resistance furnace. A helical baffle of iron wire wound around the central downtake pipe serves to break up the bubbles of benzene vapor issuing from the serrated orifice at the bottom of the downtake pipe. Preliminary experiments disclosed that the operation of such a helical baffle produced satisfactory subdivision of gas bubbles during their passage through the liquid heating medium. The mixed diphenyl and benzene vapors leave the reactor at the top through the offtake. The vapors are then conveyed through the lagged pipe to the condensing system, *D*, and the fixed gases then pass to the gas meter, *E*.

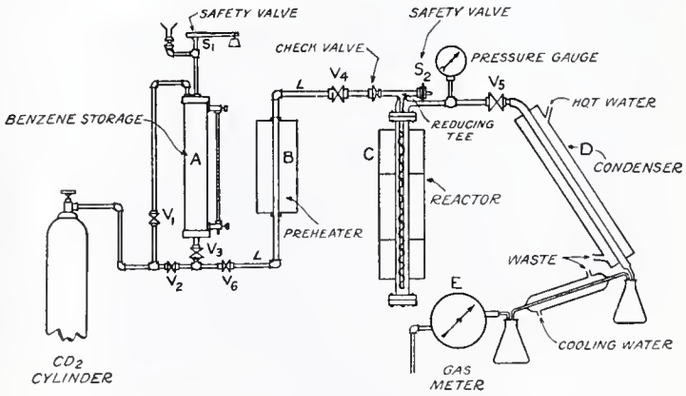


Figure 1—Diagram of Apparatus

At the beginning of a run the whole system is purged of air by means of a stream of carbon dioxide. By manipulating the valves V_1 and V_2, the carbon dioxide pressure is applied to the surface of the benzene in the reservoir. The rate of flow of the liquid benzene into the preheating vaporizer is

[1] Received March 25, 1931.

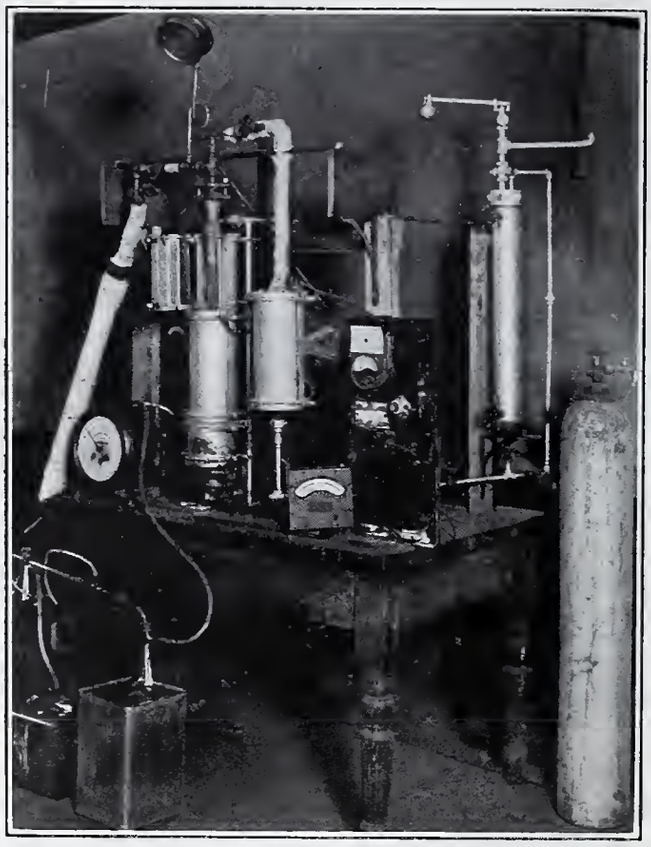


Figure 2—Apparatus Ready for Use

controlled by the valves V_3 and V_6. The temperature of the vaporizer is maintained at about 500° C. The safety valve S_1 relieves excess pressure in the reservoir. The rate of flow of benzene vapor is controlled by the valve V_4. The pyrometer junction for measuring the temperature of the reactor is shielded from the heating elements by asbestos. The safety valve S_2 relieves excess pressure in the reactor, and the outlet valve V_5 maintains the desired pressure in the reactor.

Effect of Variables on Efficiency of Method

The apparatus was employed for making characteristic test runs for producing diphenyl by this pyrolytic method, and the curves reveal the behavior under five typical sets of operating conditions, and demonstrate the influence of temperature, pressure, and rate of flow. The effects of these variables on the conversion efficiency, the chemical efficiency, and the rate of production were studied with respect to the given conditions.

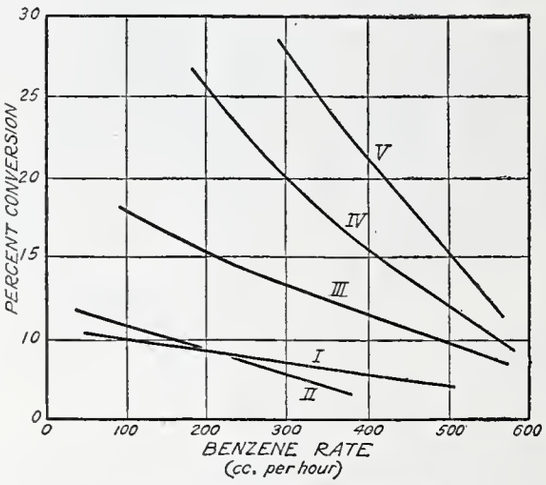


Figure 3—Conversion Efficiency

I—700° C., 1 atm. pressure
II—800° C., 1 atm. pressure
III—710° C., 100 lb./sq. in. gage pressure
IV—800° C., 50 lb./sq. in. gage pressure
V—740° C., 125 lb./sq. in. gage pressure

The conversion efficiency is the weight ratio of diphenyl to total benzene passed through the apparatus. The unconverted benzene is distilled off from the condensate for subsequent re-use. This conversion efficiency has been plotted against rates of flow for the several conditions in Figure 3. These curves indicate that the conversion of benzene into diphenyl decreases with increase in rate of flow, but that it does so less rapidly under atmospheric pressure than at elevated pressures. The conversion is increased at all rates of flow by increasing the pressure. The optimum temperature for the production of diphenyl appears to be about 740° C.

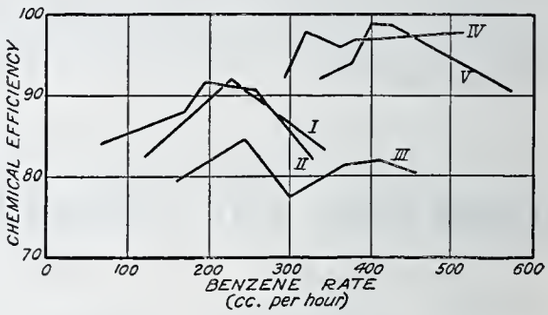


Figure 4—Chemical Efficiency

I—700° C., 1 atm. pressure
II—800° C., 1 atm. pressure
III—800° C., 50 lb./sq. in gage pressure
IV—710° C., 100 lb./sq. in. gage pressure
V—750° C., 125 lb./sq. in. gage pressure

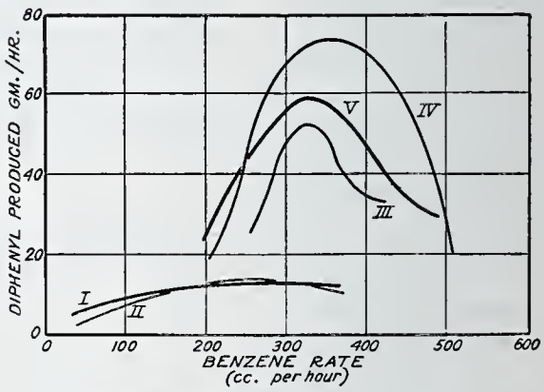


Figure 5—Rate of Production

I—700° C., 1 atm. pressure
II—800° C., 1 atm. pressure
III—710° C., 100 lb./sq. in. gage pressure
IV—800° C., 50 lb./sq. in. gage pressure
V—740° C., 125 lb./sq. in. gage pressure

The chemical efficiency is the weight ratio of diphenyl to unrecovered benzene. This figure is an index of the production of diphenyl rather than of other products. The actual values are dependent not alone upon the variables studied but upon the design of the apparatus. The chemical efficiency has been plotted against various rates of flow in Figure 4. These curves indicate that under atmospheric pressure, with moderate rates of benzene flow, chemical efficiencies in this apparatus reach maxima of 92 per cent, while with higher pressures and greater flow of liquid benzene, the maxima appear at about 98 per cent.

The rate of production is expressed in grams of diphenyl produced per hour, and is significant in determining the capacity of the apparatus. This has been plotted against various rates in Figure 5. These curves show that under atmospheric pressure and moderate rates of benzene flow, production rates of about 14 grams of diphenyl were obtained, whereas under higher pressures and somewhat greater rates of flow of liquid benzene, the production of diphenyl was about 50 to 75 grams of diphenyl per hour. It is to be noted in this connection that the volume of available space for reaction

was 10 cubic inches (164 cc.) and the depth of lead 17 inches (43.2 cm.).

Literature Cited

(1) Berthelot, *Ann. chim.*, [4], **9**, 445 (1866).
(2) Federal Phosphorus Co., French Patent 667,840 (Jan. 21, 1929).
(3) Govers, French Patent 683,230 (Oct. 12, 1929).
(4) McKee, *J. Soc. Chem. Ind.*, **23**, 403 (1904).
(5) Olgiatti, *Ber.*, **27**, 3387 (1894).
(6) Rittman, Byron, and Egloff, J. Ind. Eng. Chem., **7**, 1019 (1915).
(7) Schmidt and Schultz, *Ber.*, **5**, 682 (1872); **7**, 174 (1874).
(8) Scott, British Patent, 312,902 (June 2, 1929).
(9) Smith and Lewcock, *J. Chem. Soc.*, **101**, 1453–5 (1912).
(10) Zanetti and Egloff, J. Ind. Eng. Chem., **9**, 350 (1917).

Irregularities in Sodium Determination by Sodium Sulfate Method[1]

George W. Collins

American Medical Association, 535 North Dearborn Ave., Chicago, Ill.

OVER twenty years ago, Puckner and Hilpert (*1*) of this laboratory obtained reliable results for the sodium content of sodium diethyl barbiturate (barbital soluble U.S.P.X, known then under proprietary names of Veronal-Sodium and Medinal) by the well-known method of treatment with sulfuric acid—namely, a weighed quantity of the substance sodium diethyl barbiturate was moistened with sulfuric acid, evaporated cautiously to dryness, the charred residue ignited, and finally converted to sodium sulfate. These workers reported comparable results with two other similar methods: (1) precipitation of the barbituric acid derivative by means of diluted sulfuric acid, extraction with ether, subsequent evaporation of the acid aqueous fraction, igniting the residue, and weighing as sodium sulfate; (2) charring the substance, leaching the residue with diluted hydrochloric acid, filtering the mixture, evaporating the filtrate to dryness, and weighing as sodium chloride. In all methods examined, closely comparable results were obtained. Since then there has been occasion to reëxamine barbital soluble, and also to investigate several others of the proprietary barbital derivatives. In these investigations, whenever the product existed as a sodium salt and the sodium content was desired, the method of digestion with sulfuric acid, followed by careful evaporation and ignition, gave excellent results.

Recently, however, some irregularities have been noticed in the elaboration of standards for the identity, purity, and assay of the sodium salts of two of the isomeric amylethyl barbituric acid derivatives—namely, sodium ethylisoamyl barbiturate and two brands of sodium ethyl (*l*-methylbutyl) barbiturate, that have been introduced in medicine under various trade names. The names of the products were Sodium Amytal-Lilly, and Pentobarbital Sodium-Abbott (introduced as Nembutal) and Pentobarbital Sodium-Lilly (introduced as Sodium isoamytal). When determinations were made by the foregoing method on the preparation mentioned, the sodium content appeared to be low. These findings were communicated to the Abbott Laboratories and to Eli Lilly & Company. Both firms replied that when other methods were used, the sodium determinations were close to theoretical values. However, they did confirm the results obtained by the present investigator when using the direct "sulfate" method. Both firms, as well as this laboratory, did coöperative work on various methods. The author's results were as indicated in Table I.

The procedure for the method by extraction and sulfation shown in Table I is as follows: An accurately weighed quantity of the specimen was transferred to a suitable Erlenmeyer flask, dissolved in 50 cc. of water followed by the addition of 10 cc. of diluted hydrochloric acid, and extracted with nine successive portions of ether. The acidulated aqueous portion from the immiscible solvent extraction was transferred to a suitable tared platinum dish, carefully evaporated to dryness on the steam bath; subsequently the residue was moistened with an excess of sulfuric acid, heated cautiously on an electric heater while the fumes of sulfur trioxide were evolved, finally ignited, and weighed as sodium sulfate.

The direct sulfation method was carried out as follows: To a quantity of the specimen, accurately weighed, in a tared platinum dish are added 5 cc. of sulfuric acid, the mixture is evaporated cautiously to dryness, and the charred residue ignited. The foregoing procedure is repeated twice using 1 cc. of sulfuric acid, finally igniting, and weighing as sodium sulfate.

The procedure for the direct titration method is as follows: An accurately weighed quantity of the specimen in a 250-cc. glass-stoppered Erlenmeyer flask was dissolved in 50 cc. of previously boiled water (to remove any carbon dioxide present) and titrated with 0.1 *N* hydrochloric acid, using methyl red as an indicator.

Table I—Determination of Sodium in Sodium Salts of Isomeric Amylethyl Barbituric Acid Derivatives by Various Methods[a]

Method	Sodium Amytal-Lilly	Pentobarbital-Sodium Nembutal	Pentobarbital-Sodium Sodium isoamytal
	%	%	%
Theory	9.27	9.27	9.27
Extraction and sulfation	9.13	9.14	9.06
	9.08	9.08	9.08
Direct sulfation	8.46	8.74	8.66
	8.73	8.39	8.75
	8.38	8.44	8.38
	8.37	8.51	
Direct titration	9.14	9.06	9.03
	9.08	9.07	8.96
		9.13	9.06
		9.17	

[a] All figures calculated to dried basis.

The purpose of this paper is to point out the anomaly found in the three laboratories—namely, that the direct sulfate method gives low results in the presence of the five carbon side-chain derivatives of malonyl urea. The author is not prepared to state the exact explanation of this apparent irregularity, though there is a possibility that a portion of a sodium salt is carried over in the vapors containing isoamyl or methylbutyl compounds. It is interesting to note that after removal of the freed barbituric acid derivatives (acidification followed by an ether extraction), the sulfate method applied to the solution of the sodium salts gives accurate results, as do also titration methods.

Note—Since this article was submitted for publication, the author has noted that irregularities occur in the determination of sodium by the direct sulfate method on certain 3 and 4 carbon side-chain barbituric acid derivatives—namely, sodium ethylisopropyl barbiturate (Ipral sodium) and sodium *sec*-butylbromallyl barbiturate (Pernoston-sodium).

Literature Cited

(1) Puckner, W. A., and Hilpert, W. S., *J. Am. Med. Assocn.*, **52**, 311 (1909).

[1] Received April 6, 1931.

Analysis of Light Oils from Low- and Intermediate-Temperature Carbonization[1,2]

E. B. Kester and C. R. Holmes

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

A reliable method for analyzing light oils produced in low-temperature carbonizations has been described and its application to two series of light oils shown.

IN THE survey of the gas-, coke-, and by-product-making properties of American coals (*4*) being carried on in the United States Bureau of Mines Experiment Station at Pittsburgh, a large number of coals are carbonized at temperature intervals of 100° between the limits of 500° and 1100° C., inclusive. The light oils scrubbed from the gases in each case show an individuality determined by the particular coal carbonized and the carbonizing temperature, the differences between any two being reflected in their contents of paraffins, benzene, toluene, and other aromatics. Olefins may also be present to a degree in the crude oils, but are removed completely in the refining.

The problem of the analyst involves a determination of the relative amounts of the four components of technical significance in a particular refined light oil—namely, benzene, toluene, paraffins, and solvent naphtha. The last two terms have a specific meaning and are defined later.

Obviously, the method required must distinguish not only between classes of compounds but between homologs of the same class—that is, the aromatics—and in the presence of an undetermined number of other compounds of a different class—that is, the paraffins.

Several means of analyzing for benzene, toluene, xylene, and paraffins in mixtures are to be found in the literature. A number of them (*1, 2, 6, 8, 11, 12*) combine an arbitrary fractionation with a determination of the specific gravity of the fractions to reach this end. A variation of this method was instituted by Tizard and Marshall (*10*), who substituted the aniline point of the fractions for the specific gravity to obtain the paraffins. Unfortunately, this scheme cannot be used when the aromatics run high, as in tar oils, because such an oil is completely miscible with aniline over a wide range of temperature.

Another variation takes into account the specific gravities of the fractions before and after sulfonation (*3, 9*).

A unique attack of this problem is described by Harker (*5*). The refined oil is distilled under a Young and Thomas still-head and the volume of distillate noted for every rise in temperature of 5° from 70° to 140° C. The amounts of benzene, toluene, and xylene are estimated by comparing the distillation data with that obtained from a series of similar experiments with synthetic mixtures of the three, and in accordance with this estimate pure reagents are added to the residue in the distillation flask. The mixture is distilled as before and the volumes of distillate are compared with those of the sample. If an error has been made, the proportions are adjusted and a third fractionation is run. Paraffins present are estimated by a sulfonation test with anhydrous sulfuric acid.

Wilson and Roberts (*13*) fractionated high-temperature oils under a column and estimated the benzene, toluene, and solvent naphtha from the volume of the cuts. Paraffins were obtained by sulfonating a sample of the oil.

Recently Manning and Shepherd (*7*) have developed a method which consists briefly in (1) fractionating the oil; (2) vaporizing each fraction separately; (3) absorption of the vapor in a nitrating mixture; (4) evaporating to dryness; (5) weighing the nitro compounds; and (6) calculating the aromatics by multiplying by an appropriate factor. Although those writers have shown this procedure to give reliable results on synthetic mixtures, it appears to be somewhat time-consuming.

When paraffins are present in small quantities, as is the case when carbonization is carried out at 900° C. or above, the combination, already referred to (*1, 2, 6, 8, 11, 12*), of rectification and the specific gravity of the fractions so obtained may be used to determine the percentage of paraffins as well as that of each aromatic. The method described in the Gas Chemist's Handbook (*1*) is particularly well adapted to this purpose. On the other hand, if the carbonization temperature is 800° C. or lower, the paraffins are high enough that the equations given in the reference no longer yield accurate results.

Method Adopted

Satisfactory results were obtained by enlarging upon the method of analysis of light oils recommended in the Gas Chemists Handbook (*1*). The oil to be examined is first fractionated under a column conforming to the specifications on pages 402 and 403, and cuts taken after the directions beginning on page 403, as follows:

1—to 79°, pre-benzene
2—79–81°, benzene
3—81–109°, benzene-toluene
4—109–111.5°, toluene
5—111.5–137°, toluene-xylene
6—Above 137° (residuum). Contains xylene alone and paraffins in case of synthetic mixtures, although other aromatics also may be present, in case of light oils.

The amount of each fraction is corrected by proportionating the distillation loss among all six according to their respective volumes. Numbers 1 and 2 are combined because they consist of benzene and paraffins only.

By simply sulfonating a portion of each fraction (20 cc. is usually taken) with 3 volumes of 98 per cent sulfuric acid in a Barrett funnel, the content of aromatics is easily obtained. When no further evolution of heat or reduction in volume of the oil is noticed, the sulfonation is generally complete, but care must be taken with those fractions containing benzene that sufficient time is allowed, as this compound sulfonates with greater difficulty than its homologs. A sulfonation, however, should not consume more than 30 minutes, provided that the sulfonation of the benzene fraction is encouraged at the start by gently warming the mixture.

A determination of the aromatic content of the several cuts having been carried out, it remains only to ascertain the volume of each aromatic in those fractions where two are

[1] Received March 30, 1931. Presented before the Division of Gas and Fuel Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

present—namely, in the benzene-toluene and the toluene-xylene intermediates. To accomplish this end, 30 cc. of each intermediate are subjected to a distillation test according to the directions on page 406 of the Gas Chemist's Handbook.

If aromatics only were present, the percentage of toluene in each case could be found directly from the curves on pages 407 and 408 (here reproduced as Figures 1 and 2) by reading the value on the abscissa corresponding to the thermometer reading when exactly 15 cc. has distilled. With paraffins present, the percentage read is modified by multiplying by the percentage of aromatics in the fraction to give the true percentage. In so doing, it is necessary to assume that the paraffins are equally distributed throughout the boiling range of the intermediates.

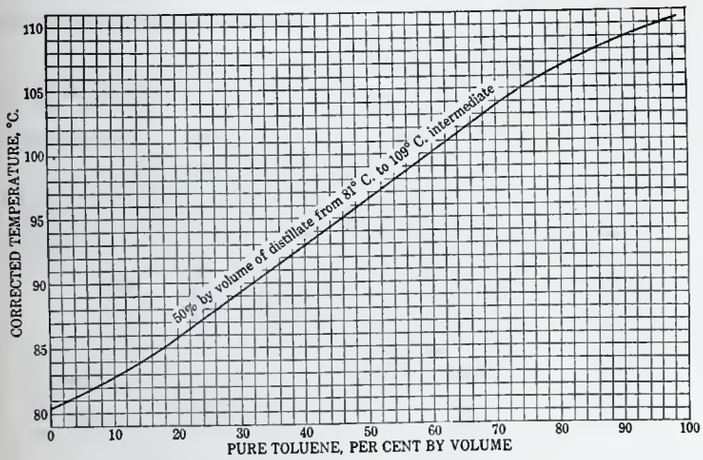


Figure 1—Benzene-Toluene Intermediates

Benzene and xylene in the respective intermediates are obtained by difference between the per cent toluene and total aromatics. A summation of the fractional percentages of each constituent gives the total present in the light oil.

Experimental Procedure

Synthetic Mixtures—To test the reliability of this method, synthetic mixtures were made up from c. p. benzene, toluene, xylene, and paraffins from gasoline having a maximum boiling point of 150° C. All olefins and aromatics were carefully removed from the gasoline with fuming sulfuric acid, after which it was distilled up to the 150° C. temperature limit.

Table I lists the results on six synthetic mixtures. On samples H, J, and K the percentages of benzene and toluene by the specific-gravity method mentioned were carried out for the sake of comparison. It may be seen that the departures from the true values are too great to be tolerable.

Table I—Analysis of Synthetic Mixtures

Mixture	Paraffins	Benzene	Toluene	Xylene
	%	%	%	%
D:				
Calcd.	29.7	21.1	49.2	
Found	29.1	22.2	48.7	
F:				
Calcd.	23.2	40.7	10.1	25.9
Found	22.2	41.5	12.1	24.2
G:				
Calcd.	20.0	26.7	26.7	26.6
Found	20.7	26.6	26.6	26.1
H:				
Calcd.	20.0	33.3	26.7	20.0
Found	19.3, 19.4, 19.0	34.0, 32.6, 34.4	27.4, 27.8, 27.1	19.3, 19.4, 19.0
By specific-gravity method		31.8, 29.1	29.1, 26.1	
J:				
Calcd.	20.0	20.0	26.7	33.3
Found	19.9	20.0	25.3	34.8
By specific-gravity method		17.8	26.4	
K:				
Calcd.	33.3	6.7	33.3	26.7
Found	34.2	7.7	31.9	26.2
By specific-gravity method		4.1	36.6	

Table II—Analysis of Light Oil from Carbonization of Davis Coal (C-Series)

Temp.	Olefins	Naphthalene	Refined Light Oil	Composition of Dry, Refined Light Oil: Paraffins	Benzene	Toluene	Solvent naphtha
° C.	%	%	%	%	%	%	%
500	14.4	..	75.3	41.00	7.4	9.3	42.3
600	18.7	..	66.3	26.5	10.3	17.4	45.8
700	10.5	0.19	78.8	13.3	15.9	26.9	43.9
800	12.6	0.01	76.4	7.9	23.4	36.1	32.6
900	8.7	0.03	83.1	3.7[a]	39.2[a]	31.1[a]	26.0[a]
1000	7.9	0.59	90.4	2.9[a]	40.4[a]	27.7[a]	29.0[a]
1100	8.2	0.48	84.9	3.0	49.0	15.7	32.3

[a] Values obtained by specific-gravity method.

Light Oils—In the survey of the gas-, coke-, and by-product-making properties of coal conducted by the Bureau of Mines, 80-pound (36.28-kg.) charges of coal are carbonized in cylindrical retorts under varying degrees of temperature. When the tar has been condensed, the gas is scrubbed with straw oil and from the latter the light oil is recovered by steam distillation. This operation, however, results in a certain proportion of the straw oil coming over. It is removed by dry distillation under a short lagged column by cutting at 200° C. The distillate at this point is called dry, crude, light oil and is reported in gallons per ton.

The crude oil is refined by shaking with sulfuric acid (70 cc. of 1.84 acid per liter of oil) to remove olefins. The mixture must be kept cool during this operation to prevent loss of aromatics through sulfonation. This treatment is followed by steam distillation and the oil so obtained is reported as dry, refined, light oil in gallons per ton.

Table III—Analysis of Light Oil from Carbonization of Mary Lee Coal (F-Series)

Temp.	Olefins	Naphthalene	Refined Light Oil	Composition of Dry, Refined Light Oil: Paraffins	Benzene	Toluene	Solvent naphtha
° C.	%	%	%	%	%	%	%
500	11.8	..	87.5	47.9	18.8	11.7	21.6
600	18.2	..	67.8	31.5 35.1[a]	17.1 9.6[a]	21.7 25.6[a]	29.7 29.7[a]
700	11.8	..	88.0	9.5 15.7[a]	26.5 23.7[a]	36.3 32.9[a]	27.7 27.7[a]
800	11.2	..	88.5	3.9 9.6[a]	32.3 29.0[a]	37.5 35.1[a]	26.3 26.3[a]
900	9.9	..	89.9	1.2[a] 0.4	57.7[a] 58.3	23.4[a] 23.6	17.7[a] 17.7
1000	5.4	..	93.7	0.5[a] 0.9	79.6[a] 76.2	11.4[a] 11.4	8.5[a] 8.5
1100	11.7	0.69	86.2	1.8[a] 0.5	73.4[a] 74.4	5.7[a] 5.9	19.1[a] 19.2

[a] Values obtained by specific gravity. In case of oil produced at 800° C. or lower, these are entered for comparison only.

The analyses of two series of light oils produced at carbonization temperatures of 500° to 1100° C. are given in Tables II and III. Coals from the Davis (Garrett County, Md.) and Mary Lee (Flat Top Mine, Jefferson County, Ala.) beds were the respective sources. For light oils from the 500°, 600°, 700°, and 800° runs the sulfonation method described in this paper was used, but above those temperatures the shorter specific-gravity method was employed. The sulfonation method was also used on the 1100° oil of the Davies series because the volumes of fractions 2 and 4 were too small to permit specific-gravity determinations. In certain cases the results from both methods are entered. It will be seen that close checks are obtained in the case of oils produced at 900° C. or higher, but there is considerable variation at 800° C. or lower where the paraffins become appreciable. The values obtained by the specific-gravity method on these low-temperature oils are entered for comparison only and are not to be considered as significant.

In these tables, the term "paraffins" is to be understood as meaning the unsulfonatable portion of the dry, refined, light

oil appearing in fractions 1, 2, 3, and 4, plus the unsulfonatable portion of

$$\text{Fraction 5} \times \frac{\text{toluene content of fraction}}{\text{aromatic content of fraction}}$$

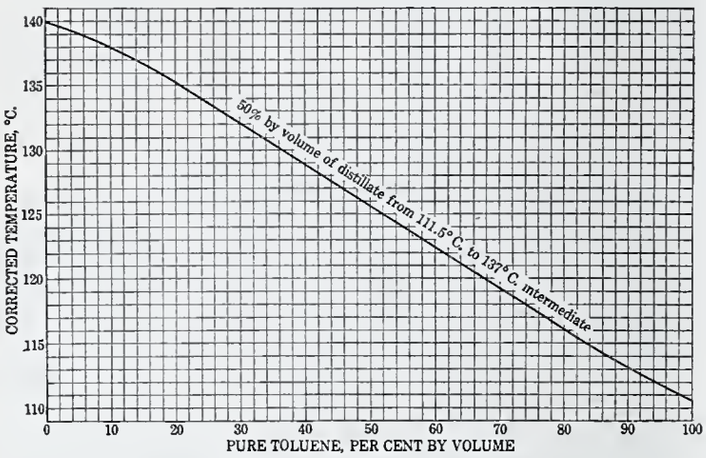


Figure 2—Toluene-Xylene Intermediates

Solvent naphtha is reported as the difference between 100 and the sum total of the benzene, toluene, and paraffin percentages.

It is clear that paraffins include only those members of the series that are in the distillate containing benzene and toluene, and small additional amounts may appear in the solvent naphtha. This arbitrary distinction was made to render the method in strict conformity with the Handbook method and produce parallel results. If desired, the classification could be altered somewhat to include in the headings, "Paraffins, Benzene, Toluene, and Other Aromatics," in which case the benzene and toluene would be determined as above, the paraffins by sulfonating a sample of the dry refined oil, and other aromatics by difference between 100 and the sum of the other three.

Acknowledgment

The writers are indebted to J. D. Davis of the Bureau of Mines Coal Research Laboratory for providing the series of light oils for analysis.

Literature Cited

(1) Am. Gas Assocn., Gas Chemist's Handbook, p. 408, 420 Lexington Ave., New York, 1929.
(2) Colman, H. G., *J. Gas Lighting*, **129**, 196–8 (1915).
(3) Colman, H. G., and Yoeman, E. W., *J. Soc. Chem. Ind.*, **38**, 82–3T (1919).
(4) Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., U. S. Bur. Mines, *Tech. Paper*, in preparation.
(5) Harker, G., *J. Proc. Roy. Soc. N. S. Wales*, **50**, I, 99–105 (1916).
(6) James, H. W., *J. Soc. Chem. Ind.*, **35**, 236–40 (1916).
(7) Manning, A. B., and Shepherd, F. M. E., Fuel Research Board (England), *Tech. Paper* **28**, 1930.
(8) Sperr, F. W., and Kohr, A. A., *Gas World*, **67**, 146–7 (1917).
(9) Thole, F. B., *J. Soc. Chem. Ind.*, **38**, 39–43T (1919).
(10) Tizard, H. T., and Marshall, A. G., *Ibid.*, **40**, 20–5T (1921).
(11) Weiss, J. M., J. Ind. Eng. Chem., **10**, 1006–12 (1918).
(12) Wheeler, E. G., and Spielman, P. E., *J. Soc. Chem. Ind.*, **35**, 396–9 (1916).
(13) Wilson, D., and Roberts, I., *J. Gas Lighting*, **134**, 225–7 (1916).

Determination of Olefin, Aromatic, and Paraffin Hydrocarbons in Neutral Oil from Coal Tar[1,2]

E. B. Kester and W. D. Pohle

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

A simple and rapid method for the estimation of olefins and aromatics in tar distillates has been described and shown to give reproducible results on samples of both known and unknown composition.

In a comparative study (*7*) of the behavior of coals when carbonized under different conditions of temperature, it became necessary to scrutinize the composition of the tars formed more closely than was possible under standard routine procedures. It was particularly desired to estimate the relative amounts of olefin, aromatic, and paraffin compounds produced at each temperature to interpret properly the secondary effects that are known to take place when carbonization is carried out at elevated temperatures.

Methods Available

The method to be used must meet two requirements: First, it must be a reliable method of approximation; second, it must not be too involved or too lengthy an operation. Close limits of accuracy are not to be expected from any method because of the wide diversity of compounds in tar distillates.

In the petroleum industry such determinations have been of great interest and importance. Many methods and variations thereof have been tried and used, some of which have been shown to be subject to gross errors. In 1925, Ormandy and Craven (*13*) suggested treatment of the oil with 80 per cent sulfuric acid, followed by a distillation to the end point of the original oil as a method for the determination of the olefins in the oil.

Kattwinkel's method (*10*) consisted in first removing both olefins and aromatics of a benzene distillate with 3 volumes of a mixture of 30 grams of phosphorus pentoxide in 100 cc. of concentrated sulfuric acid, and then estimating the olefins alone from a fresh sample of oil with concentrated sulfuric acid containing 5 grams of boric acid per 100 cc. That this method is far from accurate may be seen from Table 9 on page 357 of the reference given.

By the method of Arnold (*2*), who investigated the olefin and aromatic contents of primary tars, the former group was estimated by removal with a saturated mercuric acetate solution, while the total olefins and aromatics were determined by treating a fresh sample of the fraction under study with two volumes of methyl sulfate. No data on synthetic mixtures are given.

Brame and Hunter (*3*) investigated the composition of cracked distillates. Their determination of olefins depended on the per cent loss to 85 per cent sulfuric acid in a Babcock

[1] Received December 23, 1930. Presented before the Division of Gas and Fuel Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

bottle, and of aromatics on the aniline-point method of Tizard and Marshall (*15*).

They then fractionated the original oil, brominated each fraction, distilled to remove unbrominated compounds, and recovered the unsaturates by debromination with the zinc-copper or aluminum-mercury couple. The unbrominated portions were treated with 4 volumes of 98 per cent sulfuric acid and again with 2 volumes to ascertain the aromatic content.

The method used by Mighill (*12*) for estimating olefins in a gas oil consisted in treating a volume of the oil with twice its volume of concentrated sulfuric acid. The mixture was shaken in a bath of ice water during the treatment and then centrifuged, the reduction in volume representing the olefins. The aromatic content was obtained by treating the unattacked oil with fuming nitric acid. No data are given on known mixtures. In this procedure the use of concentrated sulfuric acid would remove some at least of the aromatics in addition to the olefins. The Bureau of Mines laboratory has found that a petroleum distillate containing 13.5 per cent aromatics when subjected to this treatment suffered a loss of 18.5 per cent of its aromatic content.

Egloff and Morrell (*4*) used 80 per cent sulfuric acid in their method for determining olefins because it has little effect on the aromatics. The unattacked oil is washed and distilled to the end point of the untreated oil, the total loss in volume from the acid treatment and the distillation being taken equal to the volume of olefins present, from which the percentage is calculated. The aromatics are determined by treating the distillate with a special nitrating mixture. The volume of nitrated compounds so obtained is multiplied by a factor which gives the percentage of aromatics present. The nitro-layer method for the determination of aromatics in tar distillates, however, is not accurate in that it can be used only in the case of limited concentrations of aromatics (*14*). Also, the volume of the nitro layer varies with the particular aromatics present (*5*).

The results obtained by Egloff and Morrell on synthetic mixtures containing benzene, toluene, amylene, octylene, and paraffins from gasoline treated to remove the olefins and aromatics, are shown in Table I.

Table I—Determination of Olefins and Aromatics according to Egloff and Morrell

	Sample 1		Sample 2		Sample 3	
		Found		Found		Found
	%	%	%	%	%	%
Olefins	12.5	16.0	16.6	21.2	20.0	18.2
Aromatics	12.5	12.7	16.6	16.9	20.0	22.7

Lomax and Pemberton (*11*), following the suggestion of Ormandy and Craven (*13*), treated the low-boiling fractions of cracked spirits with 80 per cent sulfuric acid, distilling the unabsorbed oil to the original end point. The distillate was treated with 98 per cent sulfuric acid and again distilled to the original end point. The residue remaining after this distillation was explained on the grounds that the initial treatment with 80 per cent sulfuric acid did not completely absorb or polymerize the olefins present. In their work on a cracked spirit having a maximum boiling point of 95° C., Lomax and Pemberton found that the residuum after the final distillation amounted to as much as 4.9 per cent of the original oil. Similar results appeared in the 95–125° and 125–170° fractions.

Howes (*9*) points out that in the 80 per cent sulfuric treatment, some polymers may form which will not have a boiling point high enough to cause them to remain with other polymerized products in the residuum from the distillation, and the calculations for the olefins will be correspondingly low.

Griffith (*8*) treated tar distillates with 2 volumes of 80 per cent sulfuric acid to remove the olefins, washed with water, caustic soda, and finally with water, and distilled to the end point of the original oil. The difference in volume before and after this treatment was considered due to the removal of unsaturated hydrocarbons. A portion of the distillate from this treatment was then shaken with $2^1/_2$ volumes of 96 per cent sulfuric acid, and from the contraction the percentage volume of aromatics was calculated. No data are given on known mixtures.

It is rather doubtful if 96 per cent sulfuric acid is strong enough to remove all the aromatics, because this laboratory has found that a sample of petroleum distillate containing 13.5 per cent aromatics lost only 70 per cent of its aromatic content on 5 minutes' shaking with the required volume of 96 per cent acid. The mixture was warmed during agitation. The recommendation was made by Griffith that all light oils boiling below 180° C. should be removed and examined separately.

The latest and most accurate method for the olefin and aromatic determination on petroleum distillates is that of Faragher, Morrell, and Levine (*5*). In this method the total olefins and aromatics are first determined by treatment with 91 per cent sulfuric acid, followed by a distillation to a point 5° above the original end point of the oil, and a further treatment with 98 per cent sulfuric acid. The total reduction in volume represents the total olefins and aromatics. The latter alone are then obtained by first removing the olefins from a fresh sample of oil with sulfur monochloride, nitrating with a special nitrating mixture, and removing the aromatic nitro compounds with 95 per cent sulfuric acid. Tables of analyses of known mixtures are given, showing that the method will give accurate results on a petroleum oil whose total olefin and aromatic content does not exceed 50 per cent. However, if this total is above 50 per cent, the error in the olefin percentage, which a given error in the aromatic content of the olefin-free oil will cause, increases as this total rises toward 100, if the ratio of aromatics to olefins is high as in tar distillates.

Few, if any, of the neutral oils of coal tar contain less than a 60 per cent total of olefins and aromatics and, therefore, such a method would be likely to lead to appreciable errors. Furthermore, sulfur monochloride produces so viscous a solution when shaken with tar distillates that the errors introduced from losses in handling become large. It also reacts with naphthalene and anthracene.

The Egloff and Morrell method (*4*) might have proved satisfactory except that the nitro layer becomes miscible with the paraffins when the concentration of the former is too high or too low. If the nitration is then followed by a treatment with 95 per cent sulfuric acid to remove the nitro compounds, the acid layer turns so viscous and gum-like that an accurate separation is impossible.

Method Adopted

One hundred cubic centimeters of neutral oil are shaken with 300 cc. of 80 per cent sulfuric acid for 5 minutes and permitted to stand 30 minutes before the acid is drained off. It is then allowed to stand another 30 minutes in case additional acid should separate, which is also drawn off. The reduction in volume, R_1, is recorded and the oil distilled to a point 5° higher than the end point of the untreated oil. To the volume of distillate is added a small correction factor which may be considered a constant for oils of a given boiling range and which is computed in the earlier runs from the total volume distilled, minus the total volume of distillate and residuum. After this correction is made, the volume reduction, R_2, from distillation is determined, computed to the whole oil basis, and added to R_1. From the sum, the percentage of olefins is obtained.

Twenty cubic centimeters of distillate are then shaken with 60 cc. of 98 per cent sulfuric acid for 5 minutes and allowed to

Table II—Analysis of Synthetic Mixtures

Analysis	Olefins Calcd.	Olefins Found	Olefins Diff.	Aromatics Calcd.	Aromatics Found	Aromatics Diff.	Paraffins and Naphthenes Calcd.	Paraffins and Naphthenes Found	Paraffins and Naphthenes Diff.	End Point of Paraffin Oil Used
	%	%	%	%	%	%	%	%	%	%
1	31.8	31.5	−0.3	45.2	46.3	+1.1	23.0	22.2	−0.8	240
		31.1	−0.7		46.9	+1.7		22.0	−1.0	
2	37.2	37.4	+0.2	36.6	36.6	0.0	26.2	26.0	−0.2	205
3[a]	16.3			37.2			46.5			240
4	33.8	32.6	−1.2	34.7	36.4	+1.7	31.5	31.0	−0.5	240
5	35.0	33.9	−1.1	43.4	44.8	+1.4	21.6	21.3	−0.3	240
6	19.95	19.0	−0.95	45.55	46.4	+0.85	34.5	34.6	+0.1	240
7	24.0	23.7	−0.3	41.2	42.1	+0.9	34.8	34.2	−0.6	240
8	37.2	38.3	+1.1	36.6	36.5	−0.1	26.2	25.2	−1.0	240
9	16.3	15.0	−1.3	37.2	38.6	+1.4	46.5	46.4	−0.1	240
	16.3	15.3	−1.0	37.2	38.2	+1.0	46.5	46.5	0.0	

[a] Faragher, Morrell, and Levine method caused polymerization during the sulfur monochloride treatment to such an extent that continuation of experiment was impossible.

settle as in the 80 per cent treatment. From the contraction, 0.19 cc. is deducted in the case of known mixtures, because this represents the solubility of the paraffins in 98 per cent sulfuric acid. The corrected value, r_3, is then computed to the whole oil basis from the equation

$$R_3 = \frac{r_3 \times (\text{orig. vol.} - R_1 - R_2)}{V_3}$$

where V_3 is volume of oil used for the aromatic determination, and R_3 the volume of aromatics in the original sample.

Table II lists the results obtained in the analysis of known mixtures. Analysis of sample 2, containing benzene, toluene, xylene, paraffins, and cyclohexene, was made after the Faragher, Morrell, and Levine method, but when it was applied to sample 3 which contained styrene, indene, naphthalene, xylene, and paraffins, polymerization became so pronounced that even an approximate separation into layers could not be obtained. Knowns of the same composition as samples 2 and 3 appear in 8 and 9, respectively, and were analyzed according to the procedure just described, as were also samples 1, 4, 5, 6, and 7. The latter group was made up from cyclohexene, indene, styrene, benzene, toluene, xylene, naphthalene, and a paraffin oil having an end point of 240° C.

Table III—Analysis of Distillate of 1000° Tar

Sample	Olefins	Aromatics	Total
	%	%	%
1	27.4	72.1	99.5
2	26.1	72.8	98.9

Table IV—Olefins and Aromatics in Neutral Oil of Tar Distillate, Elkhorn Series

(Max. distillation temp., 300° C.)

Temp. and Run	Olefins	Aromatics	Total
	%	%	%
500°, A-17	12.5	50.3	62.8
600°, A-15, 16	13.1	56.0	69.1
700°, A-7	18.2	74.5	92.7
800°, A-12	18.9	78.3	97.2
900°, A-2	18.6	80.6	99.2
1000°, A-21, 22	16.0	82.8	98.8
1100°, A-5	15.6	83.7	99.3

The mixed-type compounds, such as styrene and indene, were calculated as olefins, as they are removed with the purely olefinic substances by the initial treatment with 80 per cent sulfuric acid. That they are regarded as aromatics by some is recognized by the writers, who admit the deficiencies of the method in failing to classify them as a separate group.

It will be observed that the olefins as a rule are consistently low. This is possibly owing to incomplete polymerization of the olefins by 80 per cent sulfuric acid. The high aromatic contents are a result of this and the solution of certain paraffins in the concentrated acid or in the acid solution of aromatic sulfonic acids.

This method of analysis, although not so accurate as might be desired, yields a fair estimate of the olefins, aromatics, and paraffins in a tar oil, which was the end sought. As a routine analysis in the survey of the gas-, coke-, and by-product-making properties of American coals, it consumes a minimum of time and gives consistent results. That these results are reproducible is seen from the duplicate determinations on samples 1, 9, and the identical pair, 2 and 8.

On the distillate of a 1000° tar having a maximum boiling point of 350° C., an analysis in duplicate gave the results shown in Table III.

Table V—Olefins and Aromatics in Neutral Oil of Tar Distillate, Roda Series

(Max. distillation temp., 300° C.)

Temp. and Run	Olefins	Aromatics	Total	Av. Olefins	Av. Aromatics	Av. Total
	%	%	%	%	%	%
500°						
B-12	9.4	53.4	62.8			
B-11	10.2	54.7	64.9	9.8	54.0	63.8
600°						
B-13	14.1	67.8	81.9	14.1	67.8	81.9
700°						
B-10	16.3	74.4	90.7			
B-9	15.1	78.5	93.6	15.7	76.4	92.1
800°						
B-2	17.1	77.5	94.6			
B-3	16.4	76.0	92.4	16.7	76.7	93.4
900°						
B-4	16.2	80.3	96.5			
B-5	11.5	84.8	96.3	13.5	82.9	96.4
B-8	12.9	83.7	96.6			
1000°						
B-6	15.7	83.0	98.7			
B-15	18.2	80.6	98.8	16.9	81.8	98.7
B-20[a]	16.6	82.9	99.5	16.6	82.9	99.5
1100°						
B-7	18.4	80.0	98.4			
B-17	19.3	79.8	99.1	17.7	80.5	98.2
B-16	15.5	81.8	97.3			

[a] Mixture of Roda, Dunbar, and Derby not computed in average.

Table VI—Olefins and Aromatics, Elkhorn Series

(Percentages on dry-tar basis; max. distillation temp., 300° C.)

Temp. and Run	Olefins	Aromatics	Naphthenes and Paraffins	Total Olefins and Aromatic
	%	%	%	%
500°, A-17	4.6	18.4	13.6	23.0
600°, A-15, 16	4.6	19.4	10.7	24.0
700°, A-7	7.0	28.5	2.8	35.5
800°, A-12	6.3	26.1	0.9	32.4
900°, A-2	5.7	24.7	0.3	30.4
1000°, A-21, 22	3.5	17.9	0.2	21.4
1100°, A-5	2.9	15.5	0.1	18.4

Analysis of Neutral Oil from Tar Distillates

Analyses were carried out on the neutral oils in the tar distillates from the carbonization tests on Roda (*1*) and Elkhorn (*6*) coals, the series ranging from a 500° C. carbonization temperature to 1100° C. In some cases less than 100 cc. of neutral oil were available. No correction for the solubility of the paraffin fraction in the 98 per cent sulfuric acid was made because the composition of the tars vary widely from one carbonization temperature to the next, and an extremely small quantity of paraffins is available for running these solubility determinations from the neutral oils of high-temperature carbonization tests. The correction factor for the neutral oil of a low-temperature tar obtained from a carbonization of Roda coal in a rotating Fischer retort at 500° C. amounts to 0.5 cc. If this is applied to all the neutral oils in the series, the aromatic content as found would be lowered by about 2 per cent of the values given and the paraffin content correspondingly raised.

Tables IV and V give the percentage of olefins and aromatics in the neutral oil of the two series of tars, the difference between the total and 100 being the percentage of paraffins and naphthenes. Tables VI and VII show these percentages computed to a dry-tar basis.

Table VII—Olefins and Aromatics, Roda Series

(Percentages on dry-tar basis; max. distillation temp., 300° C.)

Temp. and Run	Olefins	Aromatics	Naphthenes and Paraffins	Total Olefins and Aromatics	Av. Olefins	Av. Aromatics	Av. Naphthenes and Paraffins	Av. Olefins and Aromatics
	%	%	%	%	%	%	%	%
500°								
B-12	3.2	18.2	12.6	21.4				
B-11	3.9	21.1	13.6	25.0	3.6	19.6	13.1	23.2
600°								
B-13	5.0	23.9	6.3	28.9	5.0	23.9	6.3	28.9
700°								
B-10	5.3	24.1	3.0	29.4				
B-9	5.1	26.4	2.1	31.5	5.2	25.3	2.5	30.5
800°								
B-2	5.5	24.7	1.7	30.3				
B-3	5.6	25.9	2.6	31.5	5.6	25.3	2.1	30.9
900°								
B-4	4.8	23.8	1.0	28.6				
B-5	3.4	25.3	1.1	28.7	3.9	24.2	1.0	28.1
B-8	3.6	23.4	0.9	27.0				
1000°								
B-6	4.8	25.3	0.4	30.1				
B-15	5.2	23.0	0.4	28.2	5.0	24.1	0.4	29.1
B-20[a]	4.2	21.0	0.1	25.2	4.2	21.0	0.1	25.2
1100°								
B-7	4.7	20.2	0.4	24.9				
B-17	5.6	23.1	0.3	28.7	4.8	21.5	0.5	26.3
B-16	4.1	21.3	0.7	25.4				

[a] Mixture of Roda, Dunbar, and Derby not computed in average.

Acknowledgment

The coöperation of J. D. Davis of the Bureau of Mines Coal Research Department in providing the series of tars for analysis is hereby gratefully acknowledged.

Literature Cited

(1) Am. Gas Assocn., Rept. of Sub-Committee on Survey of Gas- and Coke-Making Properties of American Coals, *Proc. Am. Gas Assocn.*, 1930.
(2) Arnold, H., *Z. angew. Chem.*, **36**, 266 (1926).
(3) Brame, J. S. S., and Hunter, T. G., *J. Inst. Petroleum Tech.*, **13**, 794 (1927).
(4) Egloff, G., and Morrell, J. C., Ind. Eng. Chem., **18**, 354 (1926).
(5) Faragher, W. F., Morrell, J. C., and Levine, I. M., Ind. Eng. Chem., Anal. Ed., **2**, 18 (1930).
(6) Fieldner, A. C., Davis, J. D., and Reynolds, D. A., Ind. Eng. Chem., **22**, 1113–23 (1930).
(7) Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., "Survey of Gas-, Coke- and By-Product Making Properties of American Coals." Bur. Mines, *Tech. Paper*, In preparation.
(8) Griffith, R. H., "The Analysis of Gas Oils and Hydrocarbon Oils from Tars," Am. Gas Assocn., Rept. of Sub-Committee on Evaluation of Gas Oils, p. 9, 1930 Convention; *J. Soc. Chem. Ind.*, **48**, 252T (1929).
(9) Howes, D. A., *J. Inst. Petroleum Tech.*, **16**, 54 (1930).
(10) Kattwinkel, R., *Brennstoff-Chem.*, **8**, 353–358 (1927).
(11) Lomax, E. L., and Pemberton, E. S., *J. Inst. Petroleum Tech.*, **12**, 57 (1926).
(12) Mighill, T. A., *Am. Gas Assocn. Proc.* **1458** (1927).
(13) Ormandy, W. R., and Craven, E. C., *J. Inst. Petroleum Tech.*, **11**, 533–6 (1925).
(14) Riesenfeld, E. H., and Bandte, G., *Erdöl und Teer*, **2**, 491 (1926).
(15) Tizard, H. T., and Marshall, A. G., *J. Soc. Chem. Ind.*, **40**, 20T (1921).

Scorching, and Other Plasticity Changes in Rubber Compounds on Heating[1]

E. O. Dieterich and J. M. Davies

Physical Research Laboratories, The B. F. Goodrich Company, Akron, Ohio

A method is described which employs the Goodrich plastometer for detecting the initial stages of vulcanization of uncured rubber compounds. Reduction in plasticity, at standard room temperature, of test pieces previously heated for various intervals at selected temperatures is used to determine the degree of cure and thus to estimate safe operating temperatures and periods. Examples of the application of the method to a variety of compounds are presented. Other temperature effects, such as heat stiffening and softening, which have not previously been reported, are illustrated.

In the study of the temperature coefficient of plasticity of compounded rubber stocks with the Goodrich plastometer (*1*), it was observed that frequently an abrupt drop in plasticity values occurred at temperatures surprisingly low as compared with those of factory cures. This suggested that the instrument might easily be adapted to the estimation of the scorching tendencies of different compounds. This note will describe the methods adopted for demonstrating the changes in plasticity which take place at temperatures corresponding to those of mixing mills and calenders. Since it is intended only as a description of experimental methods the general nature only of the stocks used in illustration will be given; detailed reports of the behavior of accelerators, retarders, etc., are planned for future publication.

The literature on rubber contains frequent references to methods of measuring relative scorching of accelerated mixes. This has been reviewed by Thies (*3*) who proposed that the relative solubilities of compounds at the end of various periods be used as an index of the degree of cure and thus afford a means of comparing the activities of accelerators. It does not appear that this method has any advantages in economy of time and material over plastometric measurements such as used by Krall (*2*) and adopted by several laboratories, nor does it afford the exactness possible with the latter method. As pointed out by other observers (*4*), the Williams plastometer is less sensitive than the Goodrich instrument, so we might expect the latter to bring out small differences which would be obscured in tests on the former. Moreover, since the Goodrich plastometer measures two factors, softness and retentivity, the exact nature of the changes produced by heating are easily visualized. It is generally, but not invariably, true that both the softness factor and the retentivity vary in the same way with different treatments of the same compound.

Three methods have been used in this study.

Method 1—The temperature coefficient of plasticity is measured. The differences in the curves for compounds which set up at relatively low temperatures and those which do not are shown in Figure 1. The sharp break in curve 3 at a temperature near 90° C., and the marked decrease in plasticity above this temperature are evidence that the stock has been cured fairly tight in the preheating time of 30 minutes, the time required to assure that the test pieces are uniformly warmed throughout. The other two curves, one

[1] Received April 7, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

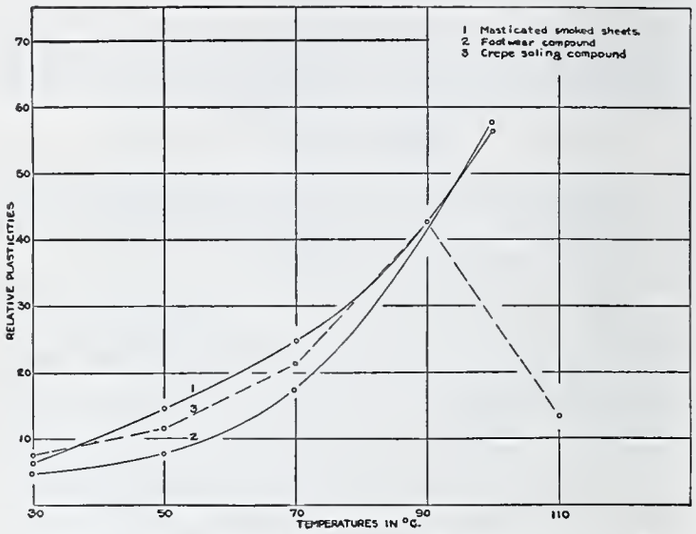


Figure 1—Temperature Coefficients of Plasticity for Three Rubber Compounds

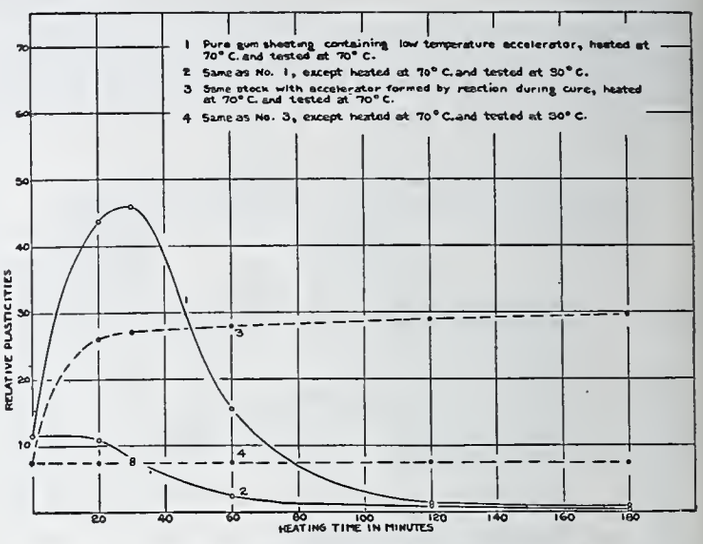


Figure 2—Comparison of Two Methods of Measuring Scorching of Rubber Compounds

for crude rubber and the other for a slow curing compound, follow the normal course expected for these stocks. This method, however, does not lend itself to locate accurately either temperature or time of the beginning of cure, but it does afford a means of rough comparison between different compounds.

Method 2—The test pieces are heated in the plastometer furnace for intervals up to 3 hours at selected temperatures, and plasticity measurements made in the usual fashion. The types of curves obtained by this method are given in Figure 2, curves 1 and 3. If the stock is non-scorching at the testing temperature, the plasticity rises and remains at constant value after the test piece is thoroughly heated, for the duration of the heating period, as illustrated by curve 3. If the stock tends to scorch, however, the plasticity values show a sharp decrease with or without a period of constant plasticity. The behavior of such a compound is illustrated by curve 1. Here again the location of the onset of cure is difficult to measure with accuracy, for this involves the determination of the deviation of the time-plasticity curve from the normal course of the curve representing the stock under non-scorching conditions.

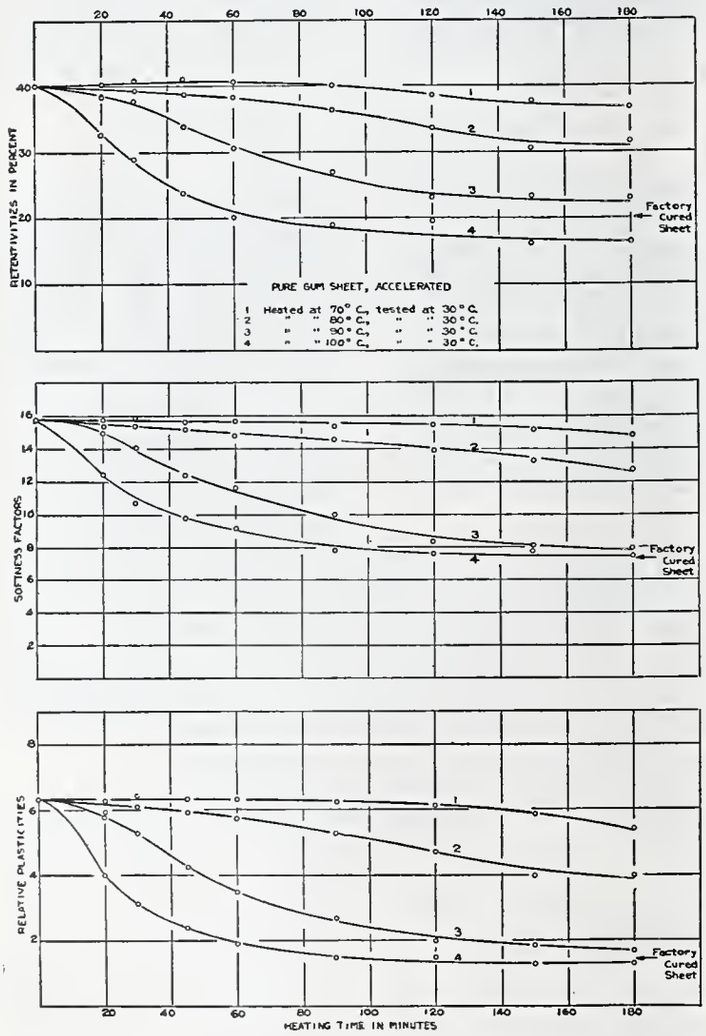


Figure 3—Time-Temperature Changes in Retentivity, Softness Factor, and Plasticity of Accelerated Rubber Compound

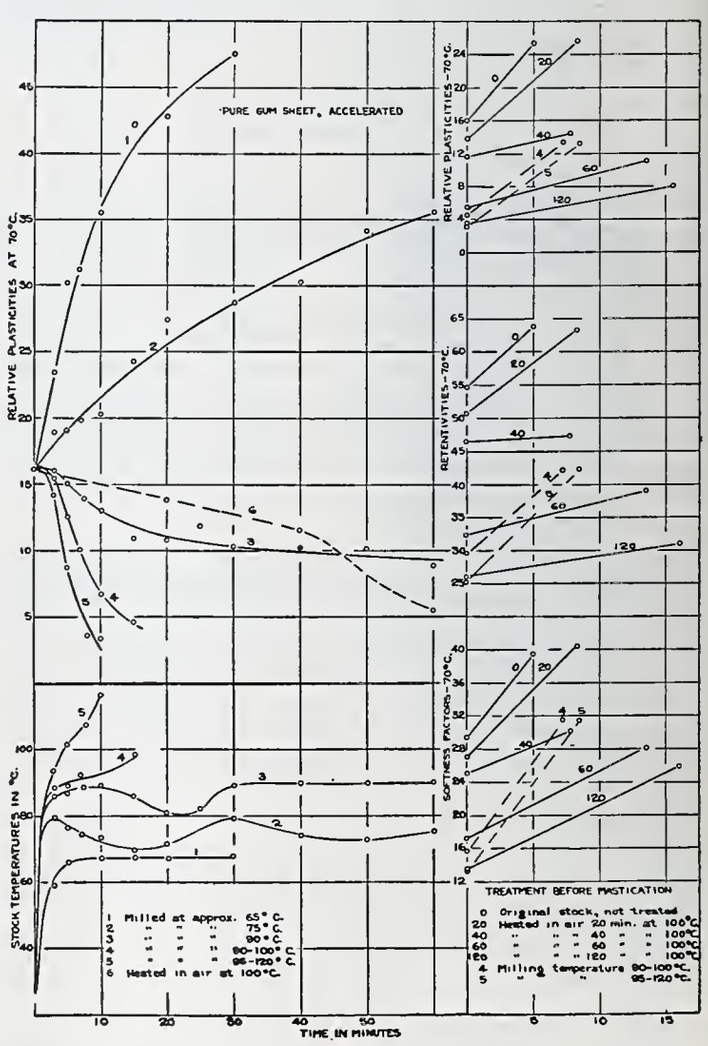


Figure 4—Milling Tests for Rubber Stocks Scorched by Prolonged Heating and by Milling

METHOD 3—The test pieces are prepared and heated at selected temperatures for various intervals in an air oven, quickly cooled, and then tested at room temperature which has been standardized at 30° C. (86° F.). If no change has occurred, the plasticity values will lie along a horizontal line parallel to the time axis. Deviations from this line downward generally indicate that cure has taken place, and the length of time elapsing before such departure is a measure of the safe time of storage at the temperature of test. Figure 2, curves 2 and 4 represent a scorching and a non-scorching compound, respectively, heated at 70° C. (158° F.), and correspond to curves 1 and 3 in the same figure. The definiteness of the beginning of cure in curve 2 as compared with curve 1 is well illustrated by this example.

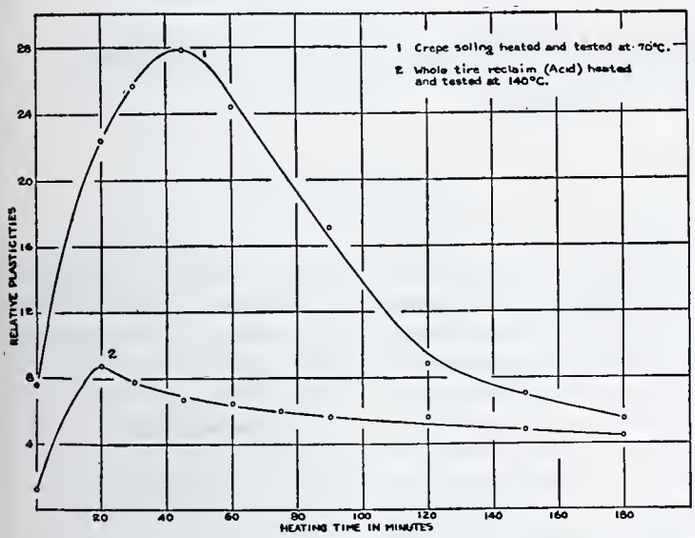


Figure 5—Comparison of Curing Effect and Heat Stiffening in Rubber Compounds at Elevated Temperatures

Unless the compounds are air-curing, the results are not affected if the test pieces are not measured immediately upon thorough cooling. For certain stocks measurements made as long as 24 hours after cooling have shown the same values as those made less than an hour after cooling.

For convenience it is preferred to preheat the test pieces in a mold in an air oven. The mold consists of a steel tray containing a series of bars in which are drilled holes just slightly larger than the diameter and slightly deeper than the height of the test pieces. In the apparatus used, each bar can accommodate twelve test pieces and is stamped at the end with the number corresponding to the interval of preheating. In this way a number of compounds, up to six, may be simultaneously heated and conveniently removed at the proper time. During the preheating, the mold is closed by a heavy steel lid to prevent longitudinal distortion of the test pieces. Before loading, the mold is brought to the desired temperature, either in a platen press or in the air oven.

Comparison of Results

In general it has been found that, for a given compound, the progress of the changes in the softness factors, retentivities and plasticities, follows the same course for different treatments, such as mastication and aging, although this is not invariably true. An illustration of this behavior in cure is given in Figure 3 in which the parallelism of the three factors is evident. It may be noted that the factory cure for this compound is the equivalent of 45 minutes at 144° C. (280° F.), yet at 100° C. (212° F.) a definite cure has occurred within 20 minutes. As judged by the downward deviation of the plasticity-time curves, storage at 70° C. (158° F.) for any long interval would be decidedly detrimental to the calendering properties of the compound, approximately 2 hours being the safe time limit.

Practical Application

The translation of the observed plastometric effects into factory operations is of great practical importance. For example, for the highly accelerated compound illustrated in Figure 3, the mixing time is 26 minutes for 50-pound (22.68-kg.) batches on 60-inch (1.52-meter) mills, the roll temperature of which is specified not to exceed 52° C. (125° F.). The temperature of the warm-up mills is maintained at the same figure. Calender temperatures are not allowed to exceed 88° C. (190° F.) and small feeds are specified. Under these conditions the stock may be processed successfully.

It is also of interest to note that the plasticity factors for this compound in the form of the factory-cured product are equal, within the limits of production variations, to those of the test pieces heated for about two hours at 100° C. (212° F.). It has been stated that the most important difference between vulcanized and unvulcanized rubber lies in the disappearance of the plastic state of the material; it has been found, however, that all the compounds so far studied possess measurable plasticity in the cured condition.

Milling and heating tests for samples from factory-mixed batches of this compound are illustrated in Figure 4. The lower left-hand curves represent the temperature changes in the stock when milled in 1-kg. (2.2-pound) batches on small laboratory mills, 15 × 30 cm. (6 × 12 inches). The corresponding plasticity changes are shown by the group of curves in the upper left-hand portion, with the addition of a curve showing the changes produced by heating in air at 100° C. The end points for curves 4 and 5 corresponding to milling periods of 10 and 15 minutes at 90° to 120° C. represent badly scorched stocks. This is equally true of the batch heated 60 minutes at 100° C., curve 6.

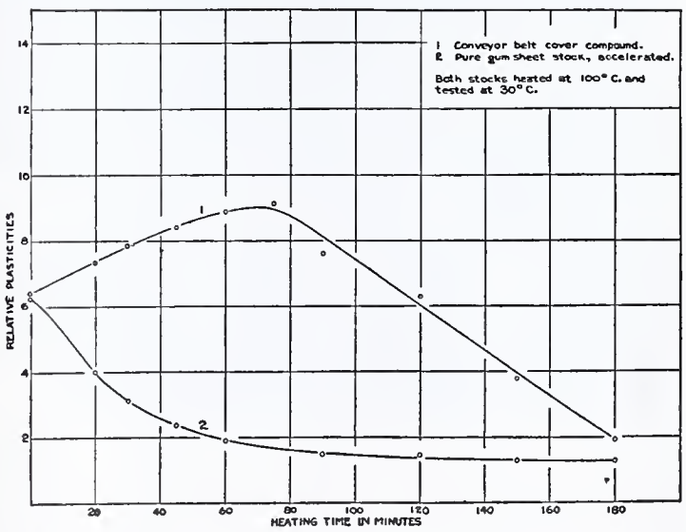


Figure 6—Heat Softening Followed by Stiffening Compared with Usual Scorching at 100° C.

The plasticity increases produced in these batches upon further mastication and cooling are shown in the curves in the right-hand portion of Figure 4. It is at once evident that the effects produced by heat and by milling at high temperatures are not of the same nature, as indicated by the rate of change of plasticity factors. In the case of the batches scorched by milling, the rates of increase are approximately the same as for the original stock, while for the batches heated in air from 20 to 120 minutes, the rate of plasticizing is progressively reduced as the time of heating becomes longer. Moreover, the retentivity factor is affected more than the softness factor—that is, on milling the stock remains more "nervy" although it appears to soften to a satisfactory degree.

Other interesting effects of prolonged heating upon the plasticities of unvulcanized rubber compounds are illustrated

in Figures 5 and 6. In Figure 5 the difference between scorching (curing) and heat stiffening is shown. Curve 2 demonstrates the gradual stiffening of a whole-tire acid reclaim. This cannot be considered cure, at least in the ordinary sense, on account of the previous devulcanization history and the low free sulfur content of the sample, approximately 0.1 per cent. Figure 6, curve 1, demonstrates another effect sometimes observed, in which the compound first gradually increases in plasticity, then, as heating continues, gradually stiffens. This, also, cannot be considered scorching such as is illustrated by curve 2 obtained for another compound under exactly similar conditions. The plasticity changes illustrated by the curves in Figures 5 and 6 are not transient effects, since at least 24 hours elapsed between heating and testing. These latter effects are generally observed in low-grade stocks of relatively low plasticities, but are nevertheless of importance in factory operations, and their elimination by proper compounding effects improvement in processing.

Literature Cited

(1) Karrer, Davies, and Dieterich, Ind. Eng. Chem., Anal Ed., **2**, 96 (1930).
(2) Krall, Ind. Eng. Chem., **16**, 922 (1924).
(3) Thies, *Ibid.*, **20**, 1223 (1928).
(4) Winkelmann and Croakman, *Ibid.*, **22**, 965 (1930).

Microturbidimeter for Determination of Rubber Content of Latex[1]

S. D. Gehman and J. S. Ward

Research Division, The Goodyear Tire & Rubber Co., Akron, Ohio

It is desirable to devise a method for determining the dry rubber content of latex which will be both more rapid than the two trial coagulation methods and more precise than the hydrometric method. The turbidity of latex, depending upon the volumetric number and size of the suspended rubber particles, offers a satisfactory criterion for the determination of the rubber content of latex. A microturbidimeter, herein described, has been adapted to such determinations. It permits more rapid determinations of the rubber content than the two trial coagulation methods. Its precision is less than the lengthy trial coagulation method, involving coagulation, creping, and drying, but is probably greater than that of the shortened trial coagulation method involving only coagulation and creping. Its precision is approximately 1 per cent rubber in 35 per cent latex.

The turbidity of latex obeys the turbidity-dilution law for rubber-content values less than 15 per cent.

The use of color filters, transmitting the shorter wave lengths of light, minimizes the effects of a difference in the effective mean particle size of different kinds of latex.

Latex, from which crude rubber is obtained by coagulation, is a white colloidal suspension of the consistency of thick cream. It consists of rubber particles of various sizes suspended in a clear straw-colored serum. The actual distribution of the particle sizes, which range usually from 0.5 to 2.0 microns, differs somewhat for samples from different sources. Although the rubber content of latex from different trees may vary considerably, 35 per cent rubber by weight may be considered a representative figure for the dry rubber content of plantation latex, collected and bulked from a large number of trees.

It is very desirable to know the rubber content of latex to facilitate its proper coagulation and to secure some uniformity in the properties of the resulting crude rubber. Since considerable latex is purchased by the crude rubber producers from various plantations, an accurate knowledge of the rubber content of purchased latex is desirable to establish a fair purchase price for the same. There are in general four methods, either in use or proposed, for the determination of the rubber content of latex—namely, trial coagulation, hydrometric, viscosimetric, and nephelometric.

Trial coagulation is the standard precision method consisting of rapid coagulation of a known amount of latex and subsequent creping, drying, and weighing of the resulting rubber. This somewhat lengthy method may be shortened with a resulting loss in precision by omitting the final drying of the creped rubber and applying an arbitrary correction for the water content of the creped rubber. The hydrometric method, using laticometers, has been subjected to considerable experimentation and has had rather wide adoption. However, this type of instrument has been found by many experimenters to give unreliable rubber determinations. The viscosity of either natural or treated latex has also been found to be an unreliable criterion for the determination of rubber content. Nephelometric methods, one of which has been suggested by Whitby (*4*), have not been fully developed and put into general practice.

Nephelometric or turbidimetric methods offer a most promising field for future development of rapid and precise determinations of rubber content. Ordinary nephelometers and turbidimeters cannot be used for the measurement of natural or moderately diluted latex because of its high turbidity. A supersensitive turbidimeter, the microturbidimeter developed and described by Conklin (*1*), for the measurement of photographic emulsions, has been slightly modified and adapted to the measurement of the rubber content of latex. Its operation is based on the extinction or obscuring of an incandescent filament by a thin film of latex contained between the spherical surface of a convex lens and a flat glass plate.

Theory

If an incandescent filament is viewed through a turbid suspension such as latex, the filament appears yellowish surrounded by a field of less intense diffuse light. As the depth of the suspension is increased, the filament becomes redder and less intense with respect to the diffuse field and disappears when the two light intensities become approximately the same. The depth of the suspension for this apparent extinction of the filament depends upon the turbidity of the suspension, which in turn depends upon the mean size and volumetric number of the suspended particles, the effective

[1] Received April 6, 1931. Presented before the Division of Rubber Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

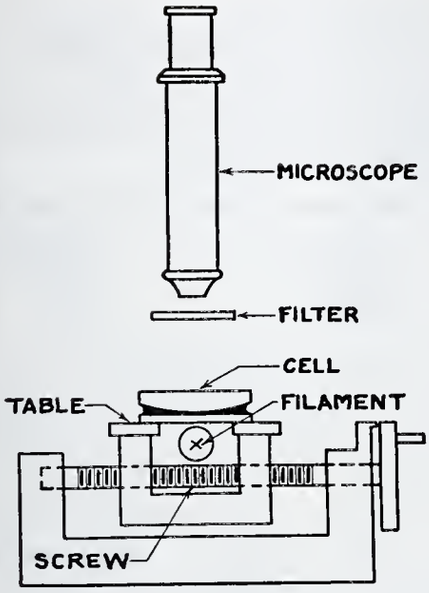


Figure 1—Microturbidimeter

mean wave length or color of the light from the filament, and the refractive indices of the two phases of the suspension. Since the rubber content of the latex depends upon the size and volumetric number of the rubber particles, this extinction principle for turbid suspensions can be used with proper precautions to determine the rubber content of either natural or concentrated latex.

For suspensions, where the concentration only is varied, the product of the concentration and the extinction depth is approximately constant—i. e., a curve plotted between the extinction depth and the reciprocal of the concentration should be an approximately straight line. Wells (*3*) gives a fuller discussion of the theory of turbidity.

Instrument Used

The microturbidimeter, shown diagrammatically in Figure 1 and as constructed for plantation use in Figures 2 and 3, consists of a microscope comparator with a traveling table

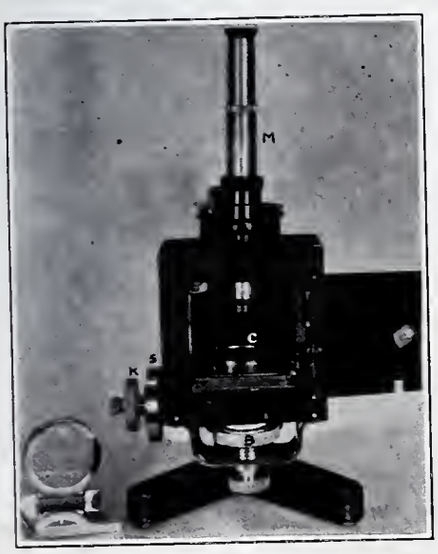


Figure 2—Microturbidimeter Constructed for Plantation Use

moved by a micrometer screw, an extinction cell containing the sample of latex, and the incandescent filament of a nonfocusing flashlight bulb operated at 1.5 volts. The extinction cell, used during most of the experimental work, consists of a small quantity of latex between the convex surface of a lens of 8.636 cm. radius of curvature and a flat glass plate. It is shown diagrammatically in Figure 4 and by photograph in Figures 2 and 3. An extinction cell using a glass biprism, with the apex flattened and having a section as shown in Figure 4, was also used. The angle of each half of this biprism is 1 degree 15 minutes.

In the experimental instrument it was possible to interpose color filters between the extinction cell and the viewing microscope. In the plantation latexometer a flat Corning glass filter, known as Sextant Green, was used as the flat plate of the extinction cell. No color filter was used for the data reported on the following curve sheets unless noted otherwise on the sheets themselves.

Figure 2 shows the viewing microscope, *M;* the extinction cell, *C*, in position on the traveling table of the comparator; the circular scale, *S*, and the knurled heads, *K*, of the micrometer screw; the base, *B*, on which the 3.8-volt flashlight bulb is mounted; and a partially opened extinction cell beside the instrument. Figure 3 shows a fully opened, and also a closed extinction cell containing latex. The dark central spot within the patch of latex of the closed cell represents a clear central spot where the lens rests in contact with the flat glass plate.

Test Samples of Latex

This investigation was restricted to the study of six samples of either preserved plantation latex or commercially concentrated latex because of our remoteness from the sources of natural latex. Two of the six samples were ammonia-preserved plantation latex received in two different shipments of commercial latex. One sample of considerable age,

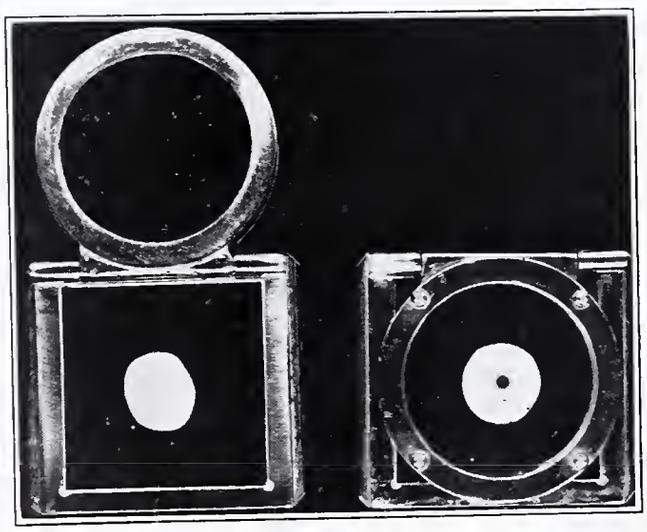


Figure 3—Extinction Cells Containing Latex

Left, fully opened cell Right, closed cell

whose exact history is unknown, had apparently concentrated in some manner to a dry rubber content[2] of 44.51 per cent during its storage in the laboratory. This concentration was probably the result of some creaming and the frequent withdrawals of samples of latex from the container. The other was a fresher sample with a dry rubber content of 37.15 per cent. The two samples of commercially concentrated latex listed as Jatex[3] were obtained from the same shipment of Jatex received from Jeavons Tinto & Company of London. Their dry rubber contents were 60.05 and 60.50 per cent, respectively. The two remaining samples of commercially concentrated latex listed as Revertex[4] were obtained from two different shipments of Revertex from the K. D. P. Co., Ltd. One of these samples of Revertex had

[2] The term "dry rubber content of latex" is used to designate the rubber content determined by coagulation, creping, and drying.

[3] Concentrated in a supercentrifuge by the Utermark process.

[4] Concentrated by evaporation.

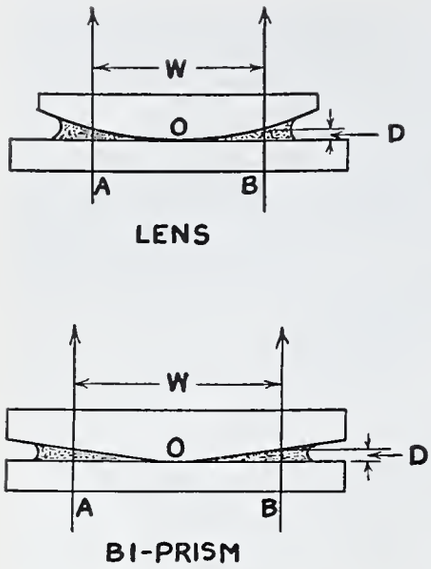


Figure 4—Extinction Cells

O, clear central spot
A and *B*, extinction points
W, extinction widths
D, extinction depths

been previously diluted to a dry rubber content of 52.44 per cent from approximately 80 per cent. The other sample was undiluted with a dry rubber content of 80.0 per cent.

Experimental Procedure

The extinction cell containing latex was placed on the traveling table of the instrument with the light bulb fixed directly under the extinction cell in the field of view of the microscope. The depth, *D*, of the optical path through the latex within the cell was varied by rotating the micrometer screw and thus shifting the cell sidewise until extinction of the light filament in the microscope field was obtained at *A* and also at *B* on both sides of the clear central spot of the cell at *O* (see Figure 4). The extinction width, *W*, for this combination of latex and cell was obtained from the two micrometer readings corresponding to extinctions at *A* and *B*. For theoretical consideration, the extinction depth, *D*, was computed from the extinction width, *W*, by the approximate formula

$$D = \frac{W^2}{8R}$$

where *R* is the radius of curvature of the lens.

Extinction or calibration curves were obtained by observing either extinction depths or widths for different known dilutions of latex of known dry rubber content, and by plotting depths or widths as a function of the rubber content of the diluted latex. In all of the data shown below, distilled water was used as diluent except where noted otherwise.

Discussion of Extinction and Calibration Curves

Numerous curves, plotted either as extinction or calibration curves, are shown and discussed to give some of the turbid properties of latex and the characteristics of this instrument as applied to latexometry.

Figure 5 gives extinction curves for Revertex using the lens and also the biprism in the extinction cell. These curves are characteristic of the curves for the other samples of latex. The extreme turbidity of latex is indicated by the fact that films of plantation latex thicker than 0.05 mm. completely obscure the incandescent filament. Extinction cells made of either a lens or the special biprism give closely comparable results. Although the geometry of the cell using the biprism is somewhat simpler than that containing the lens, the lens type of cell has been adopted because of its simplicity and convenience in practice and its easy procurability.

The straight-line portion of the curve of Figure 6, showing the relation between extinction depths and reciprocals of rubber content, indicates that the turbidity of water-diluted latex obeys the concentration-turbidity law when the rubber content does not exceed 15 per cent. This straight-line relation holds for concentrations as low as 0.002 per cent rubber content as measured with a turbidimeter using long columns of highly diluted latex.

Table I—Refractive Indices of Latex and Diluents

Material	Refractive Index
Crude rubber	1.535
Latex serum	1.341
Distilled water	1.333
Glycerol	1.474

Tolman and Vleit (*2*) have observed with a tyndallmeter a phenomenon similar to the minimum of the curves of Figure 5, or the departure from the straight line of Figure 6. No complete or satisfactory explanation of this phenomenon is offered at this time. It is possible that we are concerned with a transition from the transparent phase of water and serum to the partially transparent phase of rubber.

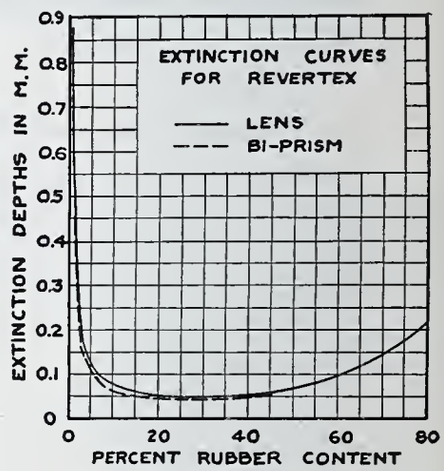


Figure 5

The curves of Figure 7 show the change in the character of the extinction curves when latex serum or glycerol is used as a diluent for latex instead of water. The use of latex serum as diluent does not eliminate the minimum in the extinction curves, but gives an extinction curve very similar to that obtained with water as diluent. Although the use of glycerol as diluent eliminates this minimum, its use as a diluent has no immediate practical value in latexometry, but may have some theoretical interest. It is interesting to note in Table I the refractive indices of the component phases of latex and these diluents.

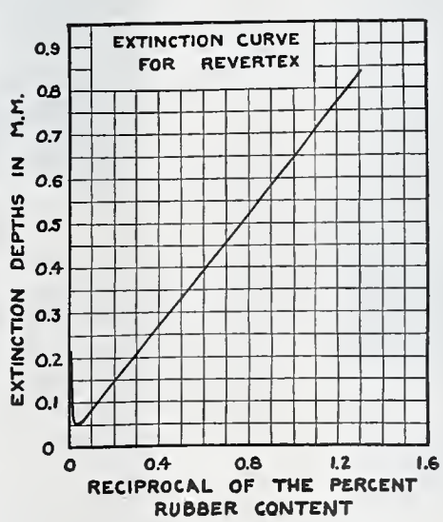


Figure 6

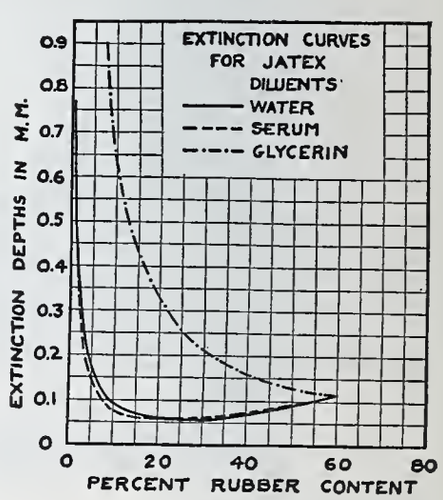


Figure 7

The slight difference in the extinction curves for water-diluted and serum-diluted latex is consistent with the slight difference in the refractive indices of water and serum. The great difference in the extinction curves for water-diluted and glycerol-diluted latex—i. e., the large decrease in the

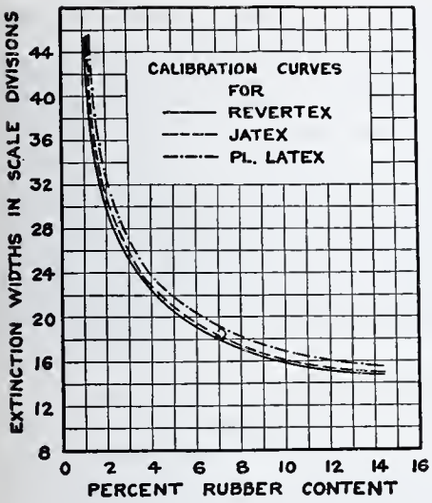


Figure 8

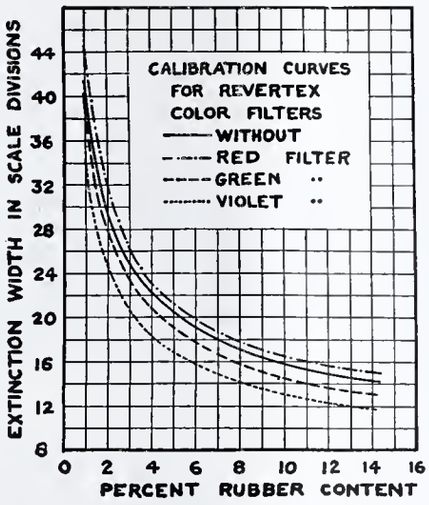


Figure 9

turbidity of the glycerol-diluted latex—is no doubt due to the large increase in the refractive index of the glycerol-diluted serum to a value near that of the suspended rubber.

The rubber content of natural or plantation latex falls in the region of the minimum of the extinction curve where two values of the rubber content correspond to a single value of the extinction depth. This would result in an ambiguity in converting values of extinction depth into rubber content, if this region of the extinction curve should be used as a calibration curve for the instrument. To avoid this ambiguity, it is desirable to use a moderate, known dilution of the unknown latex, such as a one-tenth dilution of plantation latex. It is then possible to use curves plotted between extinction widths in micrometer-scale divisions and per cent rubber content up to 10 to 14 per cent as calibration curves for the instrument as a latexometer.

Figure 8 shows the calibration curves for the two samples each of plantation latex, Revertex, and Jatex. The two samples of each type of latex—namely, Revertex, Jatex, and plantation latex—give practically identical calibration curves. The calibration curves for these six samples are therefore shown as one curve for each type of latex. The observed differences in the three calibration curves are probably due to differences in the effective mean particle size in these various types of latex—namely, natural and the two types of concentrated latex. Considerable error may be introduced in determining the rubber content of a sample of latex with an incandescent filament alone, unless a calibration curve is used for approximately the same particle-size distribution.

Since the turbidity of latex depends upon the particle size and the color of the transmitted light, it is possible to use filters to minimize this effect of particle size. Figure 9 shows the calibration curves for Revertex obtained with and without color filters. The color filters used were Wratten light filters listed as Orange Red 71 Aβ; Green (Micro-Standard Tricolor) 58 BZ; Violet 76 θ. None of these filters transmitted monochromatic light. The green and violet filters transmitted considerable red which was especially noticeable when the cell was near the extinction point. Latex becomes more turbid with less differences in its extinction owing to differences in particle size as the wave length of the transmitted light decreases.

The green filter is recommended for use in the determination of the rubber content of latex since it is more pleasing to the observer, yields a more sensitive balance than the other two filters, and decreases the spread between the calibration curves for different latices. Figures 10 and 11, giving the calibration curves for Revertex and plantation latex, obtained with and without the green filter, show this decrease in the spread of the two calibration curves. For example, let us assume that a sample of latex is submitted for test. The sample is diluted one part in ten with water and extinction widths of 24 and 22 scale divisions are observed, respectively, with and without the green filter. Without the filter, the calibration curves with a simple multiplication of 10 would indicate a rubber content of 33 or 39 per cent, depending upon the choice from the two calibration curves of Figure 10. With the green filter, the two computed values would be 34 to 35 per cent.

Discussion of Method

The judgment of the extinction of a filament through a turbid medium depends upon the visual acuity of the observer, which varies considerably for different observers. It is therefore necessary with this instrument for each observer to obtain his own calibration curve. A moderately experienced observer can duplicate his calibration curve or rubber determinations within 1 per cent for observations repeated immediately or on succeeding days. However, it may be desirable for the observer to check his calibration occasionally to avoid errors arising from pronounced changes in his own visual acuity.

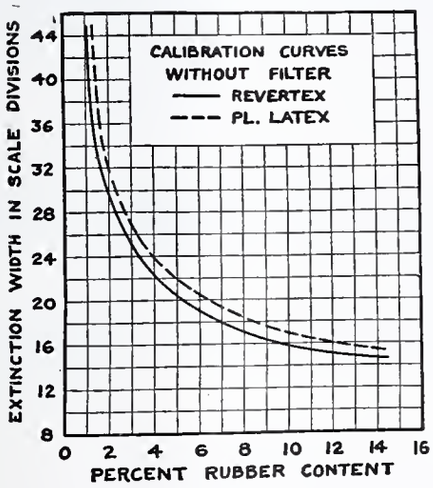


Figure 10

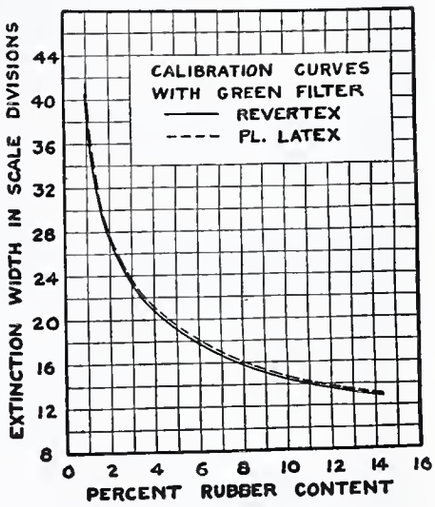


Figure 11

The effects of different visual acuities of observers may be diminished by using a photometric turbidimeter. The experimental microturbidimeter was modified to permit a photometric balance of the filament viewed through the extinction cell with an auxiliary filament viewed through a turbid filter. This was accomplished by inserting a piece of plate glass inclined 45 degrees to the axis of the microscope, between the color filter and the extinction cell of Figure 1. The auxiliary filament was so placed that this inclined glass plate superimposed the image of the auxiliary filament upon the image of the extinction filament. The procedure consisted of shifting the extinction cell until a photometric balance was obtained between the two filaments partially extinct by the extinction cell or the turbid filter.

Curves plotted between the depths for photometric balance

and the rubber content of the diluted latex, were similar in character to the extinction curves of Figure 5. This photometric type of turbidimeter is very susceptible to changes in intensity of either or both filaments. The microturbidimeter is much less susceptible to changes in intensity of the filament for latex measurements. An increase in the voltage on the 3.8-volt extinction light from 1.5 to 3.0 volts produced only a slight change in the extinction readings for latex. This change was due probably more to a change in the effective color of the filament than to a change in its intensity.

The judgment of extinction by an observer depends greatly upon the light history of his eye with respect to the intensity of light entering his eye just before making an observation. Since the extinction of the filament occurs at low light intensities, it is desirable for the observer's eye to be fully "dark adapted." Observations by a partially "light adapted" eye yield erratic results. Since the interval of "dark adaption" is considerable, the microturbidimeter should be used in a dark room or a room of low constant intensity of illumination.

The microturbidimeter with a green light filter permits the determination of the rubber content of latex with a probable precision of less than 1 per cent rubber content in 35 per cent latex. The time required for this determination is less than 5 minutes as compared with 2 or more hours for the long method involving coagulation, creping, and drying, or a probable half hour for the short method of coagulation and creping without drying. The precision is not so good as the long coagulation method, but is better than the short coagulation method.

Literature Cited

(1) Conklin, O. E., *J. Optical Soc. Am.*, **10**, 573 (1925).
(2) Tolman, R. C., and Vleit, E. B., *J. Am. Chem. Soc.*, **41**, 297 (1919).
(3) Wells, P. V., *Chem. Reviews*, **3**, 331 (1927).
(4) Whitby, G. S., "Plantation Problems of the Next Decade," paper presented before the Batavia Congress, 1914.

Methods for Detection and Identification of Synthetic Resins[1]

Theodore F. Bradley

American Cyanamid Co., Linden, N. J.

A system is presented for the detection and identification of those synthetic resins most commonly present in liquid coating compositions.

The importance of the density and the refractive index of these resins in establishing their identity has been shown. Co-relation of these values with the results of the general physical and chemical examination is accepted as the basis for their identification. Qualitative tests for halogens, sulfur, nitrogen, phthalates, phenols, vinyl esters, rosin, cumarone-indene polymers, cyclohexanones, etc., are described. Other tests which are applied comprise tests for solubility, melting point, saponification number, unsaponifiable matter, iodine value, and fusion or destructive distillation.

ALTHOUGH the cumarone and indene resins and a few rosin modifications of some phenol-aldehyde condensation products have been used for some years as constituents of paints, varnishes, and enamels, it has been but recently that synthetic resins have come into wide use in this field.

The fertile investigations of numerous chemists have resulted in the development of many new and improved resins and uses for them. As a result of these activities many coating materials containing such resins are now being manufactured and marketed in this country.

These resins are being used alone or in admixture with cellulose nitrate or acetate, and with ordinary varnish vehicles, as film-forming agents. Their use has resulted in numerous advantages over the older types of coating materials, chief among which are improved flexibility, toughness, durability, heat and light resistance, and more rapid drying characteristics.

The development of these resins has been so rapid that there is but little published information available to assist the analyst in detecting and identifying them.

As the present article is concerned primarily with those resins of proven commercial worth, and not with the bulk of miscellaneous resins to be encountered in the patent literature, and is further confined to the field of protective coatings, it would appear desirable to classify these.

In Table I are listed the various types of synthetic resins most likely to be found in modern paints, varnishes, and lacquers. The writer has further tabulated the usual and occasional constituents of these resins as gathered both from the current literature and from his own analyses. The general occurrence of these in coating materials has been listed, and, in addition, reference has been made to the general and specific literature which is considered to be of most value to the analyst. Some outstanding characteristics of each type of resin have also been listed.

In addition to those in Table I, a few other types of resins have appeared on the market and may ultimately enter into wider use in the coating field than at present seems to be the case. These resins comprise the following:

F—SULFONAMID-ALDEHYDE RESINS

A group of which the condensation product of toluene sulfonamid and formaldehyde may comprise a typical example. Usually of water-white to pale straw color and may vary from viscous liquids to hard, brittle resins or semi-crystalline solids. Some have density of order of 1.35 and refractive index of 1.596. Qualitative tests for sulfur and nitrogen may be obtained by sodium fusion. Usually have a marked odor of formaldehyde especially upon heating. Generally soluble in esters, ketones, and aromatic hydrocarbons, and insoluble in ethanol and petroleum hydrocarbons. May occur in nitrocellulose or cellulose acetate lacquers. Not at present known to occur in varnish.

G—UREA-FORMALDEHYDE RESINS

Type of water-white resin which may contain urea, thiourea, and formaldehyde in combination. Usual commercial products extremely hard and tough solids insoluble in water and all common organic solvents. Some of intermediate condensates may exist in aqueous solution and may be used as cements or adhesives. Harder grades have been found to possess density of order of 1.48 and refractive index of 1.66.

H—CYCLOHEXANONE-FORMALDEHYDE RESINS

This type may comprise reaction product of cyclohexanone or methylcyclohexanone and formaldehyde and may in some cases be modified by

[1] Received April 9, 1931. Presented before the Division of Paint and Varnish Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

other aldehydes, vinyl esters, etc. Generally of pale lemon color, of somewhat hard and brittle nature, and of wide range of solubilities in organic solvents, including ethanol and hydrocarbons and oils. For some resins density of 1.207 and refractive index of 1.544 have been determined. These yield color reaction with acetic anhydride and sulfuric acid. Upon strong fusion usually yield odor of cyclohexanones and/or formaldehyde.

Consideration of the general composition of these resins and of the fact that they are often used in admixture with cellulose esters and with one another, and in many cases are further modified by combination or admixture with various natural resins and varnish oils, would lead one to believe that their detection and identification might prove to be difficult.

The establishment of a definite system for the examination of such products has, however, shown that the present commercial grades of synthetic resins may be readily detected and identified.

In the development and application of suitable analytical methods the writer has followed as far as possible the accepted and standardized methods now in current use for the general analysis of paints, varnishes, lacquers, and like materials, such as have been so excellently compiled by Gardner (*12*).

Preparation of Material for Examination

As the material to be identified is usually present in the form of a liquid coating composition, the first step comprises the isolation of the film-forming solids in unpigmented form—i. e., the separation of pigment, solvent, and film-forming solids.

The separation of pigment may be effected by the usual methods, as by centrifuging. In the case of large quantities of coating material where the pigment is to be discarded and the vehicle alone is of interest, a simple method of effecting the pigment removal has been devised by Gutkin of the writer's laboratory. One quart of enamel, for example, is diluted with acetone and approximately 200 grams of kieselguhr to a volume of 1 gallon. This mixture is well stirred and a portion is poured into a Büchner funnel previously fitted with a medium grade of filter paper. Suction is gradually applied until an efficient filter bed has been prepared, the first portion of the filtrate then being returned for refiltration. The remainder is then filtered. If the filtrate is still cloudy it is again mixed with kieselguhr and refiltered. The residue of pigment and kieselguhr may be mixed with a fresh portion of acetone and again filtered, the second filtrate being combined with the first. If necessary the filtrate may finally be passed through a fine grade of filter paper to obtain complete and final clarification. This procedure has given excellent results especially in the case of materials containing finely dispersed or colloidal pigment. If in any case acetone is observed to cause any precipitation or coagulation of the vehicle, one may substitute a mixture of equal volumes of acetone and benzol or other efficient low-boiling solvent. The acetone or other low-boiling solvent used in this procedure is

Table I—Types of Synthetic Resins Most Commonly Found in Protective Coatings (*2, 31, 8*)

Constituents	General Characteristics	Usual Occurrence
	A—Polybasic acid poly-esters (*1, 11, 18, 19, 27*)	
Phthalic anhydride[a] Glycerol[a] Rosin[a] Higher fatty acids[a] Ethylene or diethylene glycols Pentaerythritol Other polyhydric alcohols or ether-alcohols Monohydric alcohols Benzoic acid Succinic acid Maleic acid Malic acid Citric acid Tartaric acid Congo or other natural acidic resins Adipic acid or its higher homologs	Easily saponifiable, yielding original constituents or their salts. Saponification number, generally 200 to 600. Vary from viscous liquids to hard solids. Wide range of solubilities according to chemical composition. Usually soluble with difficulty in petroleum hydrocarbons and ethanol, requiring benzenoid hydrocarbons, ketones, esters, or ether-alcohols. Some modifications soluble in petroleum hydrocarbons and in ethanol. Density, generally 1.10 to 1.42; refractive index, 1.54 to 1.59. Upon strong fusion usually yields sublimate of phthalic anhydride. May be detected by color reactions.	Nitrocellulose lacquers; enamels, varnishes, paints, primers, and surfacers; often in conjunction with aromatic hydrocarbons.
	B—Phenol-aldehyde condensation products (*10, 23, 28, 30*)	
Phenol[a] Cresols[a] Xylenols[a] Formaldehyde[a] Rosin[a] Glycerol[a] Higher fatty acids Congo or other natural acidic resins High-boiling "tar acids" Polyhydric phenols Furfural Acetaldehyde Ortho and para hydroxy Diphenyls	Not very saponifiable unless modified by large amounts of rosin or fatty acids. Vary from viscous liquids to hard, brittle solids. Solubility varies with composition and degree of condensation. A few varieties soluble in ethanol. Usually poorly soluble in petroleum hydrocarbons unless modified by large amounts of rosin or fatty acids. Usually soluble in aromatic hydrocarbons, ketones, and esters. Density, generally 1.20 to 1.28 unless modified by considerable rosin, oils, or fatty acids; refractive index, generally 1.62 to 1.69 unless modified by much rosin or oils. Often possess marked odor of phenols, cresols, and/or formaldehyde, especially when heated. Yield color reaction for phenols.	Occasionally in nitrocellulose lacquers. Varnishes, enamels, primers, and surfacers, usually in combination with China wood oil. Spirit varnishes and cements.
	C—Cumarone-indene polymers (*17*)	
Cumarone polymers[a] Indene polymers[a] Rosin or rosin ester Higher fatty acids	Non-saponifiable unless modified by saponifiable material such as rosin or fatty acids. Varnish grades usually hard, brittle solids although softer grades in use. Generally insoluble in ethanol. Soluble in acetone, many esters, and hydrocarbons. More soluble in petroleum hydrocarbons than A and B type resins. Density, generally 1.10 to 1.15 but may range as low as 1.05; refractive index, generally 1.60 to 1.66 unless modified with rosin or oils. May be detected by color reactions. May be destructively distilled with liberation of cumarone and indene.	Spirit varnishes. Varnishes, paints, and enamels, especially when maximum alkali resistance desired. Often combined with China wood oil.
	D—Vinyl polymers (*9*)	
Vinyl chloride polymers[a] Vinyl acetate polymers[a] Polystyrene Formaldehyde Cyclohexanone aldehyde	Partially saponifiable in some cases. Usually characterized by water-white or very pale straw color. May vary from rubbery, elastic solid to hard, tough solid. Generally soluble in acetone, ethyl acetate, benzene, and toluene, and insoluble in petroleum hydrocarbons. Some grades appreciably soluble in ethanol. Usually insoluble in isopropyl ether. Usually emit characteristic odor upon heating and char easily. Density, above 1.15. Vinyl acetate types characterized by very low refractive index, 1.47 to 1.48. May be detected by color reaction.	Lacquers with or without nitrocellulose. Seldom associated with oils or varnish products.
	E—Chlorodiphenyls (*16, 24*)	
Chlorinated diphenyl[a] Rosin or rosin ester Higher fatty acids	Not easily saponifiable but partially decomposed by fusion with molten caustic. Partially saponifiable if modified by rosin or oils. May vary from thin liquid to hard brittle resin or semi-crystalline substance. Has probably wider range of solubility in organic solvents than any other synthetic resin with possible exception of cyclohexanone-formaldehyde resins. Soluble in most alcohols, ketones, esters, and hydrocarbons. Melts readily to liquid of relatively low viscosity. Density, generally 1.14 to 1.80; refractive index. 1.612 to 1.71 unless modified by other resins or oils. Can be distilled readily *in vacuo*. Yields qualitative test for chlorine by sodium fusion.	Lacquers and varnish.

[a] Most common.

then removed by distillation on the water bath and may be recovered for further use.

Following the removal of pigment and the substantial elimination of any solvent used in the foregoing step, the clear, unpigmented vehicle is ready for tests. The vehicle may be either a cellulose-ester type of lacquer in which synthetic or other resins and plasticizing agents may also be present, or it may comprise a varnish, or a solution of resin in some volatile solvent.

If the material is a lacquer containing cellulose esters, it is desirable to remove these before proceeding with the analysis. In order to accomplish this, it is advisable to dilute the lacquer with benzene or toluene until no more precipitation of the cellulose ester occurs. The clear, supernatant liquid may be decanted and the cellulose ester redissolved in acetone and again precipitated with benzene or toluene. Several such treatments may be necessary. The extracted material may then be evaporated to dryness at 100° to 110° C. or, if high-boiling solvents are present, may be concentrated by a steam distillation. The dried, oily, or resinous extracts are next thoroughly extracted with petroleum ether (b. p. 55° to 75° C.). Several such treatments may be found necessary to remove diethyl, butyl, or amyl phthalates, tricresyl phosphate, rosin, and the like. The petroleum ether insolubles are reserved for further examination. Other methods for extracting resins from lacquer have been described by Gardner (*12*).

If the material is a varnish or gum solution (spirit varnish), it may best be treated by giving it a thorough steam distillation at 110° to 120° C. to remove the volatile solvents. The residue may then be dried at this temperature in an atmosphere of carbon dioxide or other inert gas. It may then be extracted with petroleum ether to remove soluble matter or assist in the elimination of the last traces of high-boiling solvents which may not have been completely removed by the steam distillation.

All drying operations should be conducted at as low a temperature as is found practicable in order to avoid polymerization or condensation of the substance, and the use of an inert atmosphere is also advisable to prevent oxidation. The addition of 0.5 per cent of α-naphthol or of hydroquinone as antioxidants may at times prove of value.

This method for the preparation of resins or vehicles for examination has been found satisfactory in many cases, but it is realized that in some instances the procedure must be varied to meet such conditions as may arise, for example, by reason of the solubility characteristics of the solids. Certain resins such as a pure phthalic glyceride or shellac would be precipitated from a nitrocellulose lacquer with the nitrocellulose by the benzene or toluene dilution as recommended. This could be ascertained by examination of the precipitated material. Such cases are the exception and not the rule, however, and merely indicate that the analyst must use considerable care in carrying out these operations.

As has been indicated, the petroleum ether insoluble portion of the film-forming solids will generally contain the synthetic resinous constituents, although one should also examine the soluble portion and determine its nature as well. This may be examined by substantially the same methods as given for the insoluble portion.

Examination of Petroleum Ether Insolubles

The dried petroleum ether insolubles which will comprise the bulk of the resinous constituents should be subjected to the following examination.

General Nature—Note the relative degree of hardness, softening point (if a solid), color, and relative miscibility at 60 per cent concentration in the following solvents: 95 per cent ethanol, benzene, ethyl acetate, butyl acetate, Cellosolve, turpentine, and V. M. and P. naphtha. If miscible with any of these, determine by further dilution whether miscibility is retained at all lesser concentrations; if not, record the dilution ratio, performing all tests at a standard temperature of 20° to 22° C. The relative miscibility of the material with acetone, toluene, and petroleum ether will have previously been observed. Other solvents may be included at the discretion of the analyst. Viscosity determinations of some solutions will at times be found helpful. When a material is found to be partially soluble in certain solvents, the soluble and insoluble portions may be separated and recovered and each portion then subjected to the general scheme of analysis. The solubility and viscosity data of Van Heuckeroth should be consulted (*31*).

Density—The density may be determined by any standard method, using great care to exclude all air bubbles. With fairly solid materials and when 4 grams or more are available, the resin may be suspended on a fine wire and the density determined on the analytical balance by displacement of water or other non-solvent liquids of known density. For less solid materials the pycnometer may be used to advantage. For very small samples of resin or small sections of dried resin or varnish films, the density may readily be determined by immersion of the sample in salt solutions of known density. This latter method has been found to be well adapted for very rapid work in routine analyses.

Refractive Index—The refractive index of the resin should be determined. While an Abbé refractometer is sometimes desirable, it has been found that for very small samples or when material is to be conserved the microscope may be employed to advantage, using the Becke or oblique illumination methods (*3*).

Whereas most standard works relative to varnish and the varnish resins have listed the densities of the natural resins, little attention has been paid to the refractive indices of these. The data for both values in the case of synthetic resins has been found to be meager. As the writer regards these values of particular advantage in differentiating natural from synthetic resins and in establishing their identity, these were determined for a number of natural and synthetic resins and are listed in Tables II and III.

Table II—Densities and Refractive Indices of Synthetic Resins

Resin	Density	Refractive Index[a]
Glycerol phthalate	1.389	1.575
Ethylene glycol phthalate	1.352	1.570
Pentaerythritol phthalate	1.390	1.584
Commercial grade modified phthalic anhydride resin (rezyl 11)	1.210	1.573
Vinyl acetate polymer	1.15	1.473
Commercial grade vinyl resin	1.18	1.480
Commercial grade toluene sulfonamid-formaldehyde resin	1.35	1.596
Commercial grade urea, thiourea-formaldehyde resin	1.477	1.660
Phenol-formaldehyde condensation product	1.21	1.647
Cresylic acid–formaldehyde condensation product	1.20	1.645
Commercial grade modified phenol-formaldehyde resin	1.10	1.545
Commercial grade modified phenol-formaldehyde resin	1.21	1.67 to 1.70
Phenol-formaldehyde condensation product	1.270	1.671
Commercial grade cumarone-indene resin	1.14	1.617
Commercial grade cumarone-indene resin	1.142	1.645
Commercial grade chlorinated diphenyl resin	1.713	1.703
Cyclohexanone-formaldehyde resin	1.207	1.544

[a] ±0.003.

Table III—Densities and Refractive Indices of Natural Resins and Their Glycerol Esters

Resin	Density	Refractive Index[a]
Rosin (grade M, wood)	1.069	1.525
Rosin ester	1.095	1.496
Congo (hard, amber)	1.059	1.545
Congo (No. 1, pale)	1.066	1.540
Manila (hard)	1.072	1.544
Manila ester	1.090	1.506
Congo ester	1.076	1.506
Damar (No. 1, Singapore)	1.062	1.515
Sandarac	1.078	1.545
Mastic	1.070	1.536
Pontianac (fine, select)	1.068	1.545
East India gum	1.087	1.537
Kauri (grade 303)	1.043	1.565
Shellac, orange (superfine)	1.152	1.516
Shellac, bleached (dry)	1.110	1.534
Congo (fused to 30% loss in wt.)	1.050	1.545

[a] ±0.003.

The density determinations were made both by the flotation and water-displacement methods as referred to water at 20° C. The refractive indices were determined by the Becke method, using indirect illumination from a 75-watt 110-volt Mazda light bulb, and a total magnification of 150 diameters. The standard liquids used for this work were prepared by A. C. Hawkins of Rutgers University, and were standardized at 20° C. and guaranteed accurate to the third decimal place.

The values as obtained are believed to be sufficiently accurate

for the intended use. Owing to the known variation in the quality of the natural resins and to the numerous modifications or grades of the synthetic resins, the data should not be considered as absolute values but primarily as a general guide to the relative position of the various resins. Minor or wide variations from these values may be expected according to the variation in the chemical composition of the resins and their degree of condensation. With full knowledge of the density and refractive-index values for the basic types of synthetic resins, it is readily appreciated that these may have quantitative as well as qualitative applications.

The data which have been obtained show the relatively narrow range of density and refractive index in the case of the common natural resins and their esters as compared to the synthetics. In view of this, the data appear of major value for detecting and identifying the synthetic resins. However, it appears that certain natural resins may perhaps be detected in this way, and that esterification of a resin such as rosin, Congo, or manila with glycerol results in a reduction in the refractive index and an increase in density. The relatively low density and high refractive index of Kauri is also of interest.

Coffignier (*5*) and Dieterich (*6*) have described at some length the physical and chemical properties of the natural resins with methods for their analysis. They have given values for the densities of a large number of the natural resins which show that all such resins, with the exception of shellac, are not substantially over 1.10 and are of about the same order as have been determined by the writer.

In Table IV the densities and refractive indices for a number of synthetic resins are given as reported in the literature, and in Table V are shown the refractive indices of some natural resins and related materials as reported in the literature.

Table IV—Densities and Refractive Indices of Synthetic Resins Reported in Literature

Resin	Density	Refractive Index	Authority
Glycerol phthalate	1.33–1.42	1.56–1.58	Kienle
Ethylene glycol phthalate	1.31–1.36	1.56–1.57	Kienle
Phenol-formaldehyde resins	1.25–1.27	1.650–1.662	Kosta
	.....	1.47–1.60	Novak and Cech
	.....	1.62–1.70	Redmond
Polyvinyl acetate	1.190	.....	Starkweather and Taylor
Urea-formaldehyde resins	1.44	1.54–1.90	Kosta, Pollak
Chlorinated diphenyl resins	1.1567–1.80	1.6125–1.6493	Penning
Cumarone-indene resins	1.05–1.15	.....	Kenny

Table V—Refractive Indices of Natural Resins Reported in Literature

Material	Refractive Index	Authority
Shellac	1.54	Chamot and Mason
Rosin	1.548	Jamin
Copal	1.528	Jamin
Mastic	1.535	Jamin
Amber	1.546	Mulheim
Amber	1.538–1.548	Kosta
Varnish, dry	1.51–1.54	Chamot and Mason
Linseed oil, dry	1.48–1.50	Chamot and Mason
Celluloid	1.53 ±	Chamot and Mason
Natural rubber	1.535	Rowland

In view of these determinations it appears that both the density and the refractive index are characteristics of the resins, which, when taken alone or in conjunction with the results of chemical tests, will lead to their rapid detection and identification.

From the available data it is concluded that if the density of a resin is above 1.15, the resin is of synthetic origin but may contain rosin, oils, or fatty acid modifying agents (shellac may in some cases attain a density of about this value). If the density lies between the limits 1.10 to 1.15, the resin may comprise a cumarone-indene polymer, shellac, or a synthetic resin of a modified type. If less than 1.10, the resin is probably of natural origin but may be a soft grade of cumarone-indene resin or some other type of synthetic resin modified by considerable rosin and oils or fatty acids.

The refractive index will further limit the possibilities and together with the density will serve to identify some resins. The solubility, color, hardness, and chemical properties may then be applied to confirm or extend the findings.

It is of interest to note that most synthetic resins possess higher refractive indices than do the natural resins, the present known exceptions being certain vinyl polymers, chiefly of the acetate type, which fall below the range of the natural resins, and some cyclohexanone-formaldehyde resins which fall into the natural resin class. Likewise it is evident that modification of synthetic resins with oils or natural resins in sufficient amounts may be expected to bring their refractive indices within range of the natural resins. In view of this it is advisable to determine the refractive index of the unsaponifiable portion of the resin as well as that of the original substance as extracted from the coating composition.

In addition to the determinations of density and refractive index for the natural and synthetic resins, the writer has determined a few values for dried or oxidized varnish films. These films were prepared from commercial varnishes of known composition, drying a small amount of each varnish at 100° to 105° C. for 24 hours. The dried films were of fairly uniform thickness, averaging 8 mils. The results are shown in Table VI.

Table VI—Densities and Refractive Indices of Dried or Oxidized Varnish Films

Varnish Film	Density	Refractive Index[a]
6-Gallon China wood oil, Congo gum varnish	1.085	1.564
14-Gallon varnish; equal parts first varnish and 22-gallon China wood oil, Amberol varnish	1.072	1.574
China wood oil spar varnish	1.048	1.566
Another grade spar varnish	1.088	1.576
China wood oil, synthetic resin varnish, marine type	1.090	1.586
China wood oil, linseed varnish, railway finish type	1.040	1.566
Oxidizing film modified phthalate resin	1.13	1.565

[a] ±0.003.

The foregoing data show that the polymerized and oxidized varnish oils (particularly China wood oil) possess densities and refractive indices well above the known values for the raw or bodied oils as originally employed in the varnish. The dried varnish films possess densities equal to or slightly greater than do the natural resins employed in their manufacture. The presence of synthetic resins tends to increase their density and also, in some cases, the refractive index.

Owing to the increased density and refractive index of varnish films in general over those of their original constituents, an increase which in many cases will tend to mask the presence of synthetic resins, it seems generally desirable to conduct such determinations on the unoxidized varnish base rather than on the dried films.

However, an extension of this work may show that such films may be used on occasion. The use of the salt solution or flotation method for the determination of density and the Becke method for the refractive index enables data to be obtained on a few small flakes of varnish or resin such as can be scraped from a coated surface with a knife. In pursuing work of this kind it is suggested that the work of Clark and Tschentke (*4*) be consulted. They have shown, for example, that dried films of linseed oil may range from 1.045 to 1.14 in density, and after long exposure to the weather may attain a value as great as 1.379. It is probable that the refractive indices of such films would also be high.

Qualitative Tests

Tests for Halogen, Nitrogen, and Sulfur—Apply the sodium fusion as directed by Mulliken (*21*). A positive test for chlorine would be most likely to indicate a chlorinated diphenyl resin especially if the resin were of alcohol-soluble nature. As the most probable alternative the resin might contain a vinyl chloride polymer. Chlorophthalic or chlorophenols might also be indicated on occasion.

A positive test for nitrogen would suggest a urea resin and a test for both nitrogen and sulfur would indicate a sulfonamid or thiourea resin.

Behavior upon Fusion—Fuse a small piece of the resin (2 to 5 grams) strongly in a Pyrex test tube over an open flame. The formation of a white crystalline sublimate upon the

upper portion of the tube is suggestive of a phthalic anhydride resin which may be confirmed by further investigation.

Note particularly the characteristic odors evolved. Acrolein, indicative of glycerol or glycerides, may often be detected. Larger amounts of acrolein will be evolved if the resin is fused with sodium bisulfate. Acetaldehyde, indicative of glycols or vinyl derivatives or of acetaldehyde resins, may often be detected, as well as the more usual formaldehyde. Phenols may likewise be detected.

The vinyl resins in particular are often observed in char upon fusion.

Following this test it will be well to distil destructively another and possibly larger portion, adsorbing the decomposition products in water for subsequent application of the usual qualitative tests for aldehydes and phenols. The use of the Gibbs reagent for phenols as described below is especially recommended. The fuchsin-aldehyde reagent is likewise of value.

Another fusion may be conducted using approximately 50 per cent of solid sodium hydroxide based upon the weight of the resin. The strong and permeating odor of capryl alcohol during this treatment is usually indicative of castor oil. Phenolic, chlorinated diphenyl, and vinyl resins will be partially decomposed by this treatment and may be detected upon examination of the decomposition products.

Most of the synthetic resins have characteristic odors which are especially strong upon fusion and with which the analyst should become familiar.

Acetic Anhydride-Sulfuric Acid Color Tests—Following this it is advisable to conduct the following color tests which have been found to be generally reliable although best confirmed by reference to the other properties as determined.

The material should be tested for rosin or rosinates by the Liebermann-Storch method. The Halphen-Hicks method may be used for confirmation. Although these reactions, especially the former, have met with some criticism, they are nevertheless of considerable value.

The writer has noted that in addition to the violet-blue coloration as given by rosin or resinates by application of the Liebermann-Storch test, cumarone-indene polymers also yield characteristic colors In the case of the cumarone-indene resins this test yielded a bright and fairly permanent pink color. This color is masked by that of rosin when present, but the color as imparted by the cumarone resins is less fugitive and after some minutes may be detected, providing the amount of rosin is not too great.

A color somewhat like that given by the cumarone resins but of deeper color (rose red) is yielded by cyclohexanone and the cyclohexanone-formaldehyde resins. This color is less permanent than that yielded by cumarone resins and within a few minutes may change from rose to a dirty orange. The use of more concentrated sulfuric acid than specific gravity 1.53, as generally used for the rosin test, tends to increase the depth of color in both cases.

When this test was applied to some vinyl resins no color was obtained. Upon filling a depression of a spot plate with the acetic anhydride solution of vinyl acetate polymer and upon adding 2 drops of concentrated sulfuric acid to it with stirring, it was found that a bluish green color was obtained which slowly changed to green. The same test was obtained from several grades of commercial vinyl resins and was not given in the absence of the acetic anhydride. This test may therefore be specific for the vinyl resins and is at least recommended for trial.

Tests for Phthalates—In the fusion test, a white sublimate of material having the typical crystalline form of phthalic anhydride may have been obtained. This is generally a positive indication of the presence of a phthalic anhydride resinous ester, but in any event must be confirmed by other tests. Suitable tests are as follows:

Resorcinol Test—Heat from 0.25 to 1 gram of the resin in a test tube with from 2 to 3 times this amount of pure resorcinol, to the boiling point of the resorcinol (205° to 210° C.) for several minutes. Cool and extract with boiling water, with agitation of the fused mass. Dilute to from 50 to 100 cc. with distilled water. Render slightly alkaline with dilute aqueous sodium hydroxide solution, when, in the event that phthalates are present, a typical greenish yellow fluorescence of fluorescein will result. This method is an adaption of that of Holde, Bleyberg, and Aziz (*15*) for phthalic acid, who have shown that the use of concentrated sulfuric acid as a condensing agent in this test, as has been generally recommended, may often lead to confusing and erroneous results owing to the fluorescent effects obtained from substances other than phthalates in the presence of this acid.

This test may likewise be applied to a few crystals (0.05 gram or more) of the sublimate which may have been obtained by strong fusion of the resin. The test is also applicable to the detection of phthalate plasticizers in lacquers, diethyl phthalate in perfumes, denatured alcohols, etc.

Phenol Test—A less sensitive but useful confirming test involves the treatment of the resin (or other form of phthalate) with phenol and a condensing agent, to form phenolphthalein. Heat 1 gram of the resin with from 2 to 3 times this amount of pure phenol and 10 drops of concentrated sulfuric acid in a test tube over an open flame until visible reaction occurs with formation of an orange or brownish orange melt. Avoid undue charring of the resin by limiting the amount of sulfuric acid and the time and temperature of the operation. After cooling the melt somewhat, extract it with boiling water, with agitation, dilute to 100 cc., and render slightly alkaline with aqueous sodium hydroxide solution. The typical pink of phenolphthalein as exhibited in alkaline solutions is a positive test for phthalates.

Since the foregoing tests are also given by simple, nonresinous phthalate esters, these should be removed from the resin by extraction with a medium in which the phthalate resin is insoluble or only slightly soluble, petroleum ether generally being satisfactory for the purpose. However, the data obtained with respect to specific gravity, refractive index, saponification number, nature of saponifiable matter, melting point, etc., may be relied upon in the hands of an experienced analyst of synthetic resins to decide definitely as to whether the material contains resinous phthalate esters.

Tests for Phenols—Most phenol or cresol-aldehyde resins have been found to contain some free phenols in varying degree. During the steam distillation of varnish bases in their recovery for analysis, the writer has observed that in the case of many which have contained phenol-aldehyde condensation products, these free phenols are present to some degree in the aqueous portion of the distillate. By examination of this or of an extract of the resin prepared by boiling several grams of the pulverized resin in 20 to 30 cc. of water, these free phenols may be detected. Some phenolic resins, particularly those which may have been very well reacted and modified by large amounts of rosin or oils, do not respond readily to this treatment and require alkali fusion with subsequent hydrolysis in order to yield sufficient phenols for their detection. The alkali treatment of Steinitzner (*29*), who boils the resin with sodium hydroxide solution or heats the resin with soda lime to liberate some phenols, or the destructive distillation in a current of nitrogen as applied by Herzog (*14*) may be used.

The writer has obtained satisfactory results by strongly fusing a mixture of 2 to 3 grams of resin with an equal weight of pulverized sodium hydroxide. The melt, after cooling, is extracted with 10 to 20 cc. of boiling water, diluted to 50 cc., filtered, rendered slightly acid with sulfuric acid, and again brought to the boil. This solution may then be examined for free phenols.

For the detection of phenols the writer has found the indophenol test of Gibbs (*13*) to be most satisfactory. The reagent for this test comprises a solution of 2,6-dibromoquinonechloroimide (Eastman) which may be prepared by agitation

of a piece of this substance about the size of a small pea with 10 to 15 cc. of distilled water until a suspension occurs. When 2 to 3 drops of the reagent are added to from 10 to 50 cc. of the aqueous extracts of the resin, prepared as described, and the solution rendered slightly alkaline (about pH 9.4) with decinormal alkali solution, a deep, bright blue coloration develops when phenols are present. The muddy pale violet color often produced by the reagent in alkaline solution should not be confused with the true phenol test yielded by this reagent.

Whereas it is true that a test of this sort may not prove that a phenol-aldehyde resinous condensation product is present, since free phenols or other substances also yielding phenols would thus behave it may be said that this comprises a useful test for qualitative purposes. It is rendered most conclusive when co-related with the other chemical and physical properties of the material in question.

The production of considerable quantities of free phenols from the resins by the destructive distillation method of Herzog may be used to obtain sufficient phenols for their isolation and identification. Fractionation of these followed by boiling- and melting-point determinations and identification as *p*-nitrobenzyl esters (*25*) appears practicable.

Quantitative Values

Determine the acid and saponification numbers. Half normal or normal solutions of sodium hydroxide in methanol may be employed for the saponification, and whenever difficulty is experienced in effecting solution, a mixture of equal parts of C. P. benzene and a normal solution of alcoholic caustic may be used.

As sodium phthalate is but sparingly soluble in methanol, the writer has often noted that during the saponification of some phthalate resins crystals of sodium phthalate appear as the saponification nears completion. These may be removed for further examination.

If the saponification number is greater than 200 it is most probable that the substance comprises, or at least contains, resinous esters of the polybasic acid type. (Coconut oil, highly oxidized oils, and some other esters may yield fairly high saponification numbers but are generally absent from the usual compositions, and in any event will have been detected by other tests.) Polybasic acid resinous esters may on occasion be present and still yield saponification numbers of less than 200, as when modified by phenolic resins or other non-saponifiable matter.

If the material has been indicated to contain or comprise resin of the polybasic acid type, it will be well to saponify sufficient material to enable the identification of the several components.

One method for effecting separation of the saponified mixture comprises the dilution of the mixture with several volumes of distilled water, elimination of the alcohol by distillation, followed by acidification with mineral acid. Upon acidifying the mixture and boiling for several minutes, the free fatty and rosin acids which may be present are liberated and may be separated from the aqueous portion. The aqueous portion is then neutralized with sodium hydroxide and the polybasic acids precipitated as metallic salts. Calcium chloride under these conditions will precipitate a portion of the phthalic acid and some other polybasic acids, including citric, tartaric, and malic acids. Ferric chloride will precipitate the phthalic acid more effectively and will also precipitate benzoic acid and a number of other acids. Lead or silver nitrates are even more effective in the order given. The metallic salts are recovered by filtration, washed, and examined microscopically. They may then be decomposed by mineral acids and the organic acids recovered for application of color tests (*22*), and after purification their melting points and neutralization equivalents determined. They may be further checked by preparation of their *p*-nitrobenzyl esters (*26*) or *p*-phenylphenacyl esters (*7*). As a means of separation and purification, the fractional sublimation as advocated by Klein and Werner (*20*) is of evident value.

The polyhydric alcohols may be recovered from the final filtrate after removal of the acids by concentration to dryness followed by extraction with absolute ether and ethanol (1:1) or other appropriate solvents.

The free fatty and rosin acids as initially liberated may be washed, dried, and examined for acid, saponification, and iodine values. Density, refractive index, thiocyanate, and hexabromide values all assist in the identification.

The iodine value of the resin should be determined, as well as that of the fatty acid and rosin constituents. The Wijs method is preferred.

The content of unsaponifiable matter should be determined, and after extracting and drying this it should be subjected to density, refractive index, melting point, solubility, and color tests. Destructive distillation as recommended by Steinitzner (*29*) or Herzog (*14*) may be advantageously applied. Likewise, in the case of cumarone-indene resins, the methods of identification as initiated by Wolff and modified by Ellis (*8*) may be employed.

Finally, a determination of the ash content and its qualitative examination is in many cases advisable. Quantitative determinations of chlorine, sulfur, and nitrogen are of value when such have been shown to be present.

Acknowledgment

The author wishes to express his appreciation for the valuable suggestions of George Barsky, director of this laboratory, in connection with the preparation of this article; to W. C. Hansen for his helpful advice on the determination of refractive indices; and to the American Cyanamid Company and the Rezyl Corporation for permission to publish this work.

Literature Cited

(1) Barry, *Ind. Chemist*, **4**, 53–6 (1929).
(2) Barry, Drummond, and Morrell, "Natural and Synthetic Resins," Van Nostrand, 1926.
(3) Chamot and Mason, "Handbook of Chemical Microscopy," Vol. I, p. 369, Wiley, 1930.
(4) Clark and Tschentke, IND. ENG. CHEM., **21**, 621–7 (1929).
(5) Coffignier, "Varnishes," pp. 12–178, Scott, Greenwood, 1923.
(6) Dieterich, "Analysis of Resins, Balsams, and Gums," Scott, Greenwood, 1901.
(7) Drake and Bronitsky, *J. Am. Chem. Soc.*, **52**, 3715 (1930).
(8) Ellis, "Synthetic Resins and Their Plastics," Chemical Catalog, 1923.
(9) Gardner, *Paint Mfrs.' Assocn. U. S., Tech. Circ.* **337** (1928).
(10) Gardner, *Ibid.*, **339** (1928).
(11) Gardner, *Ibid.*, **358**, 47–57 (1930).
(12) Gardner, "Physical and Chemical Examination of Paints, Varnishes, and Lacquer," 5th ed., Institute of Paint and Varnish Research, Washington, D. C., p. 491–850, 1930; *Ibid.*, pp. 818–28.
(13) Gibbs, *J. Biol. Chem.*, **72**, 649–64 (1927).
(14) Herzog, *Z. angew. Chem.*, **34**, Aufsatzteil 97 (1921).
(15) Holde, Bleyberg, and Aziz, *Z. angew. Chem.*, **42**, 283–4 (1929).
(16) Jenkins, McCullough, and Booth, IND. ENG. CHEM., **22**, 31–4 (1930).
(17) Kenny, *Paint, Oil Chem. Rev.*, **89**, 2, 12–15 (1930).
(18) Kienle and Ferguson, IND. ENG. CHEM., **21**, 349 (1929).
(19) Kienle and Hovey, *J. Am. Chem. Soc.*, **51**, 509–19 (1929); **52**, 3636–45 (1930).
(20) Klein and Werner, *Z. physiol. Chem.*, **143**, 141–53 (1925).
(21) Mulliken, "Identification of Pure Organic Compounds," Vol. 1, p. 10, Wiley, 1904.
(22) Mulliken, *Ibid.*, pp. 78 and 83.
(23) Novak and Cech, IND. ENG. CHEM., **20**, 796–801 (1928).
(24) Penning, *Ibid.*, **22**, 1180–2 (1930).
(25) Reid, *J. Am. Chem. Soc.*, **39**, 304–9 (1917).
(26) Reid, *Ibid.*, **39**, 124–36, 1249–54, 1727–50 (1917).
(27) Scott, Probeck and Mileti, *Paint Mfrs.' Assocn. U. S., Tech. Cir.* **370**, 437–9 (1930).
(28) Standerman and Beakes, IND. ENG. CHEM., **20**, 674 (1928).
(29) Steinitzner, *Kunststoffe*, **5**, 109 (1915).
(30) Turkington, Shuey, and Butler, IND. ENG. CHEM., **22**, 1177–80 (1930).
(31) Van Heuckeroth, *Paint Mfrs.' Assocn. U. S., Tech. Cir.* **369** (1930).

Measurement of Effect of Carbon Black on Fluidity of Printing Ink[1]

E. P. W. Kearsley and G. L. Roberts

United Carbon Company, Charleston, W. Va.

IN THE evaluation of printing inks, properties of flow are of considerable importance, as they determine to a large extent the suitability of an ink for any specific type of work. Such characteristics, in common practice, have been judged entirely by dipping a spatula into the ink and observing on its withdrawal to what length the thread of ink so produced could be extended without breaking. This method has, undoubtedly, some value to the practical ink maker, but, being only qualitative in scope, and allowing the disadvantage of individual interpretation, merits limited recognition in the laboratory.

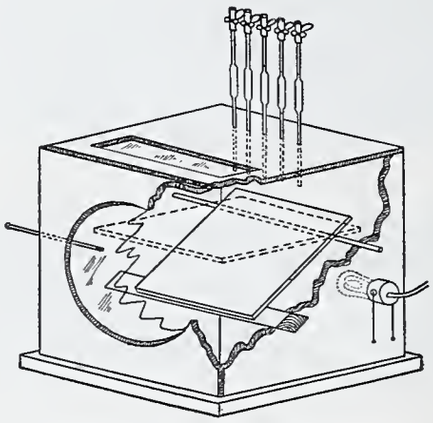


Figure 1—Diagram of Apparatus

The extensive use of carbon (gas) black in the pigmentation of printing inks has created the necessity of accurately determining its effect on the fluidity of products employing it. The designation "short flow" or "long flow" does not adequately classify a black, the distinction being quite transitional, and a wide range of blacks of equal importance to the ink maker falling between such designations. The limitations imposed by such inadequate classification of carbon blacks has stimulated this laboratory in seeking a means of determining the flow of pigment-vehicle mixtures, which would provide this information in quantitative terms. Recognizing the prime importance of adequate control and uniformity of testing conditions, as well as increased accuracy in measurement, the procedure and apparatus described below is offered as a rapid and reliable method for determining this property.

Apparatus

The tests are conducted in a box (12 × 12 × 12 inches, or 30.5 × 30.5 × 30.5 cm.) made from ordinary asbestos board, and provided in front with a door of the same material. Glass peepholes are located in the door and the top of the box to permit ease of observation and readings to be made without disturbance of temperature conditions within the box. A glass plate (9 × 9 inches, or 22.8 × 22.8 cm.) graduated longitudinally in millimeters operates on a swivel inside the box allowing it to be maintained in a horizontal position or at an angle of 30 degrees. Pipets of 10 cc. capacity inserted through holes drilled in the top of the box permit samples to be transferred to the plate.

Constant temperature carefully followed by a thermometer is maintained by means of a 60-watt carbon lamp operating in a Dim-o-lite socket of four stages of current intensity.

Method

The box is brought to a predetermined suitable constant temperature for the test by adjusting the intensity of the carbon lamp. From the data given in Table I, 45° C. was selected as being quite suitable and well within the temperature range not seriously affected by changes in seasonal atmospheric temperatures.

Exactly 0.25 gram of the pigment (carbon black) to be tested is mixed into a paste with 2.5 grams of varnish. Lithographic varnish No. 1 was chosen for our work, as this material is commonly used for testing purposes in ink laboratories. The pigment in the paste so formed is then well dispersed by four grindings each of fifty uniform circular motions with a glass muller (care being taken to apply a constant pressure), and collecting the paste together with a spatula between each grinding.

This sample is drawn into a 10-cc. pipet, the latter being then closed by means of pressure applied by a pinchcock to a piece of rubber tubing attached to the suction end, and the pipet placed in position through one of the holes provided in the top of testing box, so that the tip is about 1 inch (2.54 cm.) from the surface of the glass plate and directly over the zero graduation.

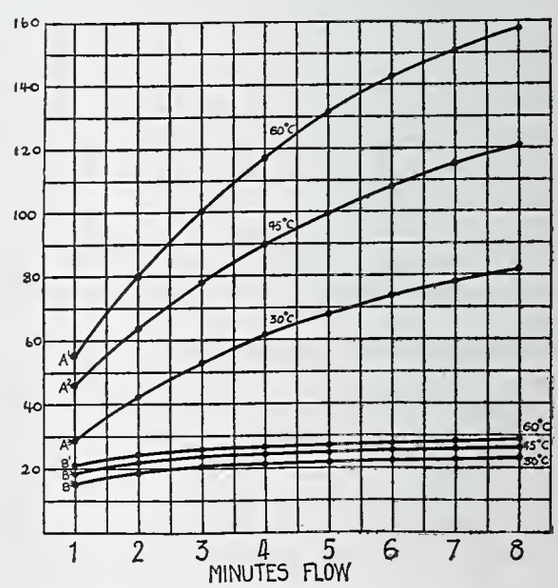


Figure 2—Effect of Time and Temperature on Flow

A preheating period of 5 minutes is allowed for the sample to adjust itself to the temperature of the box, after which the pinchcock is released, and ten drops allowed to fall from the pipet onto the surface of the glass plate which is in the horizontal position. Exactly 1 minute is given for settling of the sample after which the plate is dropped to a 30-degree angle, thus permitting the sample to flow down the plate. After 7 minutes (see note on effect of testing time), the amount of flow is measured directly from the graduations on the plate.

[1] Received April 9, 1931.

Notes on Method

Preparation of Samples—If convenient, it is suggested that a roller mill be used in place of a glass muller for the dispersion of the carbon black in the varnish medium. The authors have adopted the procedure of subjecting the paste (carbon black 1, varnish 10) obtained from a preliminary mixing to three runs of 3 minutes' duration on the roller mill. The sample thus prepared was used for the test.

Calibration of Pipets—It is very necessary, when more than one pipet is employed for this test, that every precaution be taken to assure uniformity in the magnitude of the drops delivered by them. The volume of ten drops from each pipet used should be carefully determined, and any necessary adjustment be made in the bore of the tip so as to assure the same volume being delivered from each.

Temperature of Test—Our findings indicate that the higher the temperature at which the test is conducted the greater will be the differentiation between the flow characteristics of different inks (Figure 2). The curves A^1, A^2, and A^3 represent the flow in millimeters obtained on a long-flow carbon black at 60°, 45°, and 30° C., respectively, while B^1, B^2, and B^3 show the results obtained at the same temperatures for a short-flow carbon black, from which it will be noted that the greatest difference was obtained at 60° C. A temperature of 45° C. was selected as one well served by the limitations of the size of the glass plate, and at the same time offering a range of flow between the carbon blacks likely to be examined, sufficient to allow proper classification. In addition, the seasonal changes in atmospheric temperature are less likely to effect the accuracy of the test if carried out throughout the year at a temperature slightly exceeding that experienced in the hot summer.

Time of Test—The flow time adopted for the test was selected on the basis of that point in the time-flow curves (see Figure 2) at which the effect of time on the amount of flow was uniform and at the same time gave the widest possible range of difference between samples. Seven minutes best satisfied these requirements.

Evaluation in Poises—It may be desirable to have flow information in terms of poises. A translation of results can be easily accomplished by determining this value on a standard sample with a Stormer viscometer, and running this standard with the unknown by the method suggested in this paper.

By comparison of the flow values in millimeters, the equivalent in poises for the unknown may be calculated. If necessary, the graduation of the glass plate may be made in terms of poises by the same method.

Distillation of Free Ammonia Nitrogen from Buffered Solutions[1]

M. Starr Nichols and Marian E. Foote

Wisconsin State Laboratory of Hygiene, University of Wisconsin, Madison, Wis.

A constant pH of 7.4 or above is necessary for the quantitative recovery of free ammonia nitrogen from aqueous solutions of ammonium chloride and ammonium sulfate.

When a sodium carbonate solution is used to adjust the pH, it is not possible to determine the minimum quantity necessary to maintain a pH at or just above 7.4. In fact, if such an adjustment is attempted, either the final pH will fall below the quantitative point of 7.4 and recovery be incomplete or an excessive alkaline intensity will be produced and an appreciable quantity of organic nitrogen will be included in the free ammonia nitrogen result.

A phosphate buffer of pH 7.4 has been shown to permit quantitative recovery of the free ammonia nitrogen from ammonium sulfate and chloride and yet not yield any appreciable hydrolytic property toward pure nitrogenous compounds.

In most of the wastes studied it was found that a greater recovery of free ammonia nitrogen was obtained when a phosphate buffer of pH 7.4 was used than when there was no adjustment of the pH. While it is not possible to state that a phosphate buffer of pH 7.4 does not act slightly on the organic compounds of nitrogen in wastes, its action is materially less than that of sodium carbonate.

IF THE free ammonia and organic nitrogen values of sewage and industrial wastes are to have real significance, it is imperative that a quantitative separation of these constituents be effected. For the evaluation of free ammonia, the usual procedures are either direct nesslerization or distillation. Direct nesslerization offers distinct advantages in some cases but it is not applicable to all wastes. When free ammonia nitrogen is to be determined by distillation, a standardized procedure should be followed which can be applied to various wastes to separate this form of nitrogen completely with the release of little or no organic nitrogen.

The Standard Methods of Water Analysis of the American Public Health Association (*1*) recommend the addition of 0.5 gram of sodium carbonate to waters which are acid to methyl orange in the determination of free ammonia nitrogen. The range of methyl orange extends from a pH of 3.1 to 4.4. A water having a pH of from 4.4 to 6.8 would be sufficiently alkaline to comply with the procedure given in Standard Methods. Furthermore, if a water were acid to methyl orange and 0.5 gram of sodium carbonate were added, this quantity would produce a pH of varying alkalinity, depending upon the water, up to the intensity of 0.02 *N* sodium carbonate at the beginning of the distillation and of about 0.1 *N* at the end. The pH of 0.1 *N* solution of sodium carbonate is 11.6. Again we find in Standard Methods (page 70) the caution that sodium carbonate added to sewage and effluents may give high ammonia nitrogen through hydrolysis of the nitrogenous matter; under section 4, Procedure (page 71), it is stated that if acid to methyl orange, neutralize with sodium carbonate solution. This is done, presumably, with the thought that only enough sodium carbonate solution should be added to produce an alkalinity measured in terms of pH of about 4.4. The procedure given for water would produce

[1] Received April 8, 1931. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

a high pH in most cases, while the reverse would be true for acid sewages and wastes. That these procedures are not sufficiently regulated so that an accurate measurement of free ammonia nitrogen is possible will be shown later.

The work of Phelps in 1904 (*2*), upon which the caution in Standard Methods relative to the hydrolyzing action of sodium carbonate was based, has shown that distillations carried out with the addition of sodium carbonate (concentration not stated) give a part of the nitrogen from certain nitrogenous compounds. Urea gave 2.0 per cent of the total nitrogen present, gelatin 1.4 per cent, casein 0.68 per cent, egg albumen 3.2 per cent, and peptone 1.4 per cent. Phelps also showed that sodium carbonate was active in the breaking down of some of the insoluble compounds. Samples of sewage effluents which had first been filtered through paper to remove the insoluble portion gave 7.0 per cent less free ammonia upon distillation with sodium carbonate than those which had not been filtered.

Recognizing the wide divergence in the pH values of liquids from which free ammonia nitrogen is recovered, it was decided to determine the effect of various alkaline intensities of the solution on the recovery of this fraction and evaluate the errors if such exist. The first point of attack was to determine the lowest possible pH at which free ammonia nitrogen in the form of chloride and sulfate could be quantitatively recovered, and the second to determine what amounts of organic nitrogen would be liberated at this pH and at higher pH values. In other words, would it be practical to adjust the distillation mixture with a buffer and recover quantitatively only the free ammonia nitrogen?

Adjusting Solutions

Sodium carbonate, 5 per cent solution.

Phthalate buffer 0.5 *M*. 500 cc. 1 *M* potassium acid phthalate + *X* cc. 1 *M* sodium hydroxide. Diluted to 1000 cc.

Phosphate buffer 0.5 *M*. 500 cc. 1 *M* potassium acid phosphate + *X* cc. 1 *M* sodium hydroxide. Diluted to 1000 cc.

Recovery of Free Ammonia Nitrogen from Ammonium Sulfate

In order to determine the percentage of recovery of free ammonia nitrogen at stated constant pH values, the distillation of aqueous solutions of known quantities of ammonium sulfate was conducted. Adjustment was made by using an appropriate buffer of phthalate or phosphate depending upon the pH value desired. To the flask were added the solution of the ammonium salt, 50 cc. of 0.5 *M* buffer solution, and enough ammonia-free water to make the total volume amount to 250 cc. An initial colorimetric pH reading was made before distillation was begun and a final pH reading recorded on the residual liquid in the flask after distillation was completed. A 180-cc. portion of the distillate was collected under 25 cc. of *N*/14 acid and the excess acid titrated with *N*/14 sodium hydroxide using methyl red as an indicator. The results are given in Table I.

Table I—Effect of pH on Recovery of Free Ammonia Nitrogen from Ammonium Sulfate

Nitrogen in Sample	Initial pH[a]	Final pH	Nitrogen Found	Recovery
Mg.			*Mg.*	%
20	4.9	4.6	2.2	11.0
20	5.9	5.5	6.55	32.75
20	6.4	5.9	12.45	62.25
20	6.8	6.6	18.05	90.25
20	7.4	7.3	19.8	99.0
20	8.0	7.7	19.85	99.25

[a] All samples buffered with 50 cc. of appropriate buffer to initial pH.

It will be seen that at an initial pH of 4.9 only 11 per cent of the nitrogen was recovered, with increasing quantities as the pH value of the distillation mixture was made higher. Only when the solution was adjusted with the buffer to the pH value of 7.4 did quantitative recovery exist. It seems safe to predict that any free ammonia distillation conducted below approximately this value will be in error proportional to the pH depression, initial and final.

Effect of Kind and Quantity of Adjusting Solution

After the minimum pH value for the complete recovery of free ammonia nitrogen was determined, it was then possible to measure what effect the kind and concentration of the adjusting solution had on the recovery from solutions of these ammonium salts. In these experiments a constant amount of ammonium salts was used and the quantities of the phosphate buffer pH 7.4 and the 5 per cent sodium carbonate solution were varied. The results are given in Table II.

Table II—Comparative Effect of Phosphate Buffer and Sodium Carbonate Adjusting Solution

0.5 *M* Phosphate Buffer pH = 7.4					Sodium Carbonate Solution, 5%				
Vol. buffer	Initial pH	Final pH	Nitrogen found	Recovery	Vol. soln.	Initial pH	Final pH	Nitrogen found	Recovery
Cc.			*Mg.*	%	*Cc.*			*Mg.*	%
Ammonium sulfate present equivalent to 20 mg. nitrogen									
0	7.0	4.9	1.4	7.0	0	7.0	4.9	1.4	7.0
1	7.2	3.8	5.9	29.5	0.5	8.6	5.2	8.2	41.0
2	7.4	4.7	12.0	60.0	1.0	8.9	6.0	14.3	71.5
5	7.4	6.4	19.35	96.8	1.25	9.0	6.2	17.5	87.5
10	7.4	6.8	19.6	98.0	1.5	9.1	9.8	19.6	98.0
20	7.4	7.2	19.8	99.0	1.75	9.2	9.8[a]	19.7	98.5
30	7.4	7.2	19.8	99.0	2.0	9.4	9.8[a]	19.8	99.0
40	7.4	7.3	19.8	99.0	10.0	9.8[a]	9.8[a]	19.8	99.0
50	7.4	7.3	19.8	99.0					
Ammonium chloride present equivalent to 20 mg. nitrogen									
0	6.8	5.4	1.5	7.5	0	6.8	5.4	1.5	7.5
1	7.2	4.2	7.3	36.5	0.5	8.5	3.8	7.9	39.5
2	7.4	5.0	13.2	66.0	1.0	8.8	5.9	14.1	70.5
5	7.4	6.6	19.5	97.5	1.25	9.0	6.2	16.95	84.8
10	7.4	6.9	19.6	98.0	1.5	9.1	9.6	19.6	98.0
20	7.4	7.1	19.65	98.3	1.75	9.2	9.8	19.65	98.3
30	7.4	7.2	19.8	99.0	2.0	9.5	9.8[a]	19.65	98.3
40	7.4	7.2	19.8	99.0	10.0	9.8[a]	9.8[a]	19.8	99.0
50	7.4	7.2	19.8	99.0					

[a] pH greater than this point but not determined.

From these results it is seen that, using either the phosphate buffer or the sodium carbonate solution, the concentration of the adjusting solution must be great enough to maintain the pH of the solution at approximately 7.4 or above to obtain quantitative recovery of the ammonia. While a small amount of sodium carbonate is capable of raising the initial pH to the quantitative point, the final pH drops through a wide range owing to the slight buffering action of this salt. With only 1 cc. of a 5 per cent solution of sodium carbonate, the initial pH is 8.9, somewhat above the quantitative point of 7.4, with the phosphate buffer, but the final pH is seen to drop to 6.0 with only 71.5 per cent recovery. It is evident that it is necessary to raise the initial pH to above 9.0 with sodium carbonate in order to have the final pH above the quantitative point and the recovery satisfactory. With the use of the phosphate buffer, a concentration above the necessary amount shows no effect on the initial or final pH with the recovery satisfactory. It is also evident that if an excess of sodium carbonate is used, the recovery is satisfactory but the initial and final pH values are very high.

Recovery of Free Ammonia Nitrogen from Organic Nitrogenous Compounds

In order to determine what amounts of organic nitrogen would appear as free ammonia, several organic nitrogen compounds were subjected to distillation after preliminary adjustment to a pH of 7.4 and higher pH values with phosphate buffer and sodium carbonate solution. Aqueous solutions of a number of such substances of a high degree of purity were tested. The results appear in Table III.

Table III—Recovery of Free Ammonia Nitrogen from Organic Nitrogenous Compounds

Compound	No Buffer			M/2 Phosphate Buffer pH = 7.4			M/2 Phosphate Buffer pH = 8.0			Sodium Carbonate Buffer, 5%					
				50 cc.			50 cc.			2 cc.			20 cc.		
	Initial pH	Final pH	Nitrogen recovery	Initial pH	Final pH	Nitrogen recovery	Initial pH	Final pH	Nitrogen recovery	Initial pH	Final pH	Nitrogen recovery	Initial pH	Final pH	Nitrogen recovery
			%			%			%			%			%
Ammonium chloride	6.8	5.4	7.5	7.4	7.4	99.0	8.0	7.7	99.0	9.5	9.8[a]	98.25	9.8[a]	9.8[a]	99.0
Ammonium sulfate	7.0	4.9	7.0	7.4	7.4	99.0	8.0	7.6	99.3	9.4	9.8[a]	99.0	9.8[a]	9.8[a]	99.0
Glycine	6.8	8.3	0	7.4	7.4	0	8.0	8.2	0	9.8[a]	9.8[a]	0	9.8[a]	9.8[a]	0
Asparagin	6.4	7.4	0	7.4	7.4	0.5	8.0	8.2	1.3	9.0	9.8[a]	2.1	9.8[a]	9.8[a]	5.5
Urea	5.5	7.6	2.0	7.4	7.4	5.8	8.0	8.2	9.5	9.8[a]	9.8[a]	4.0	9.8[a]	9.8[a]	8.5
Guanidine carbonate	10.4	10.8	2.5	7.4	7.4	0	8.1	8.4	0	10.8	10.8	7.0	10.8[a]	10.8[a]	8.3
Acetamide	7.2	9.3	0.5	7.4	7.4	0	8.0	8.2	0	9.8[a]	9.8[a]	3.0	9.8[a]	9.8[a]	10.0
Sodium caseinate	6.2	7.4	0	7.4	7.4	0	8.0	8.0	0	9.8[a]	9.8[a]	0	9.8[a]	9.8[a]	0
Peptone	6.1	6.4	0.5	7.4	7.4	2.0	8.0	8.2	2.0	9.8[a]	9.8[a]	2.5	9.8[a]	9.8[a]	2.5
Arginine HCl	5.4	7.2	0	7.4	7.5	0	8.0	8.2	0	9.8[a]	9.8[a]	0	9.8[a]	9.8[a]	0.5

[a] pH greater than this point but not determined.

Table IV—Effect of pH upon Distillation of Free Ammonia from Samples of Trade Wastes

Waste	No Buffer			Phosphate Buffer			Sodium Carbonate Solution		
	Initial pH	Final pH	Free ammonia	Initial pH	Final pH	Free ammonia	Initial pH	Final pH	Free ammonia
			P. p. m.			*P. p. m.*			*P. p. m.*
Raw kraut waste	5.1	5.1	8.0	7.4	7.4	80.0	9.8[a]	9.8[a]	80.0
Sand-filtered kraut waste	6.4	9.3	104.0	7.4	7.4	104.0	9.8[a]	9.8[a]	104.0
Hot pond effluent	7.1	9.8[a]	0.56	7.4	7.4	2.0	9.8[a]	9.8[a]	2.24
Main sewer catch sample	5.3	5.8	1.36	7.4	7.4	4.4	9.8[a]	9.8[a]	6.8
Sulfite waste	3.8	4.4	121.0	7.4	7.4	240.0	9.8[a]	9.8[a]	300.0
Milk waste	5.7	7.2	7.2	7.4	7.4	19.2	9.8[a]	9.8[a]	32.0

[a] pH greater than this point but not determined.

When 2 cc. of a 5 per cent solution of sodium carbonate is added to the distillation mixture, a part of the nitrogen from asparagin, urea, guanidine carbonate, acetamide, and peptone appears as free ammonia. With 20 cc. of a 5 per cent solution (1.0 gram of dry salt) still greater quantities appear, acetamide leading the group with a loss of 10 per cent of its nitrogen. Guanidine carbonate without the addition of a buffer evidences a pH of 10.4 and gave 2.5 per cent of its nitrogen as free ammonia, but with the addition of the phosphate buffer this loss was prevented. However, upon the distillation of this compound with sodium carbonate solution, it yielded 7 per cent with the smaller amount of sodium carbonate and 8.3 per cent with the larger. Aside from the result with urea, the phosphate buffer at pH 7.4 caused very little loss of organic nitrogen from these nitrogenous compounds. In this connection it will be noted that urea had an initial pH of 5.5 without the addition of any adjusting solution and it still lost 2.0 per cent of its nitrogen as free ammonia.

Recovery of Free Ammonia Nitrogen from Trade Wastes

If sodium carbonate is to be used for the liberation of free ammonia nitrogen, enough must be present to maintain a pH of 7.4 or above during the entire distillation. With some wastes this amount would be large, and the resultant pH at the beginning of the distillation would be above 10.0. This excess alkaline intensity would contribute toward the hydrolysis of the nitrogenous compounds and liberate a portion of the organic nitrogen. However, if a liberal quantity of phosphate buffer of pH 7.4 were used to maintain the pH at this point, that excess alkaline intensity would not obtain. To show the practical application of the principle of buffered distillation, a few results obtained from the distillation of certain trade wastes from solutions of different alkaline intensities are given in Table IV.

It will be noted that all the wastes used except sulfite liquor waste exhibit an alkalinity to methyl orange as indicated by their respective pH values. Yet it is seen that all of them except the sand-filtered kraut waste gave lower free ammonia nitrogen values than when they were treated with either sodium carbonate solution or the phosphate buffer of pH 7.4. In the case of this sand-filtered kraut waste the final pH rose to 9.3 which probably accounts for the high recovery from the unadjusted distillation of this waste. It is interesting to note that if free ammonia nitrogen had been determined on the sample of raw kraut waste without adjustment, only 10 per cent of the total would have been recovered. It is also noted that in all cases shown, with the exception of the kraut wastes, sodium carbonate adjustment gave higher yields of free ammonia nitrogen, and in the case of the milk waste the increase due to sodium carbonate adjustment over that found by the phosphate buffer method was 66 per cent. Since a pH of 7.4 obtained by buffering with phosphate has shown a quantitative recovery with pure ammonium salts, it seems safe to conclude that the results with phosphate buffer are more nearly quantitative.

Conclusions

(1) Sodium carbonate is not the proper adjustant for free ammonia nitrogen distillation because of its uncertain buffering action and its strong hydrolytic effect.

(2) The use of a phosphate buffer of pH 7.4 is recommended for the determination of free ammonia nitrogen by distillation.

Literature Cited

(1) Am. Public Health Assocn., Standard Methods of Water Analysis, p. 14, 1925.

(2) Phelps, E. B., *J. Infectious Diseases*, **1**, 327–40 (1904).

Copper Iron Compound Developed for Pernicious Anemia

McKesson & Robbins, Inc., has developed a copper iron compound for use in treatment of primary and pernicious anemias. The principle and results of the research work are entirely new and the Government has issued basic patents after careful investigation and the submission of clinical evidence.

Copper Determination in Organic Matter[1]

Stefan Ansbacher, Roe E. Remington, and F. Bartow Culp

South Carolina Food Research Commission and Department of Nutrition of the Medical College of the State of South Carolina, Charleston, S. C.

A critical study has been made of methods for the micro-estimation of copper in biological materials.

Organic matter can be destroyed without loss of copper in small samples by wet combustion, using sulfuric acid, perchloric acid, and fuming nitric acid. Larger samples can be burned in silica dishes at a temperature not above 400° C., followed by treatment with fuming nitric acid.

The use of ammonia to remove iron and other metals leads to results which are too high. Precipitation of copper by hydrogen sulfide is quantitative if acid concentration is properly controlled, some sulfur is precipitated with the copper and suitable precautions are taken in the filtration, washing, and re-solution of the precipitate.

On the solutions so prepared, the xanthate reagent tends to give high results, the error being least if from 100 to 200 γ of copper are present in the solution.

The carbamate reagent is applicable to solutions containing about 50 γ of copper, giving results agreeing very closely with those obtained by the chromotropic reagent, which can be used to estimate quantities as small as 2 to 3 γ with an accuracy of 0.5 γ.

The Biazzo reagent is most reliable for 50 to 150 γ of copper, but tends to give results which are slightly low. The method of preparing and using the chromotropic reagent is described in full.

SINCE copper is found to play a physiological role, chemists have been obliged to find ways and means of estimating, not only approximately but quantitatively, the small amounts of copper normally present in organic matter.

The electrolytic determination of copper generally used in chemistry is undoubtedly the most accurate method which could be employed, but it can be applied to biological material only when a huge amount of sample is taken. That is in some cases (e. g., a spleen of a new-born rat) impossible, and in other cases it is impracticable, as a great amount of organic matter must first be destroyed.

The credit for having developed a method ten years ago, which is still used, goes to Supplee and Bellis (*22*), who applied to milk Scott and Derby's (*19*) method for detecting, with potassium ethyl xanthate, traces of copper in salts crystallized in copper containers. This method, usually called the "xanthate method," was found not to be sufficiently accurate for the estimation of copper in all kinds of biological material by Elvehjem and Lindow (*8*). These investigators developed, at about the same time as Schönheimer and Oshima (*18*), a method by use of the Spacu (*21*) reaction (formation of a copper-rhodanine-pyridine complex). Usually this method is called the "Biazzo (*2*) method." A few months later, Callan and Henderson (*3*) suggested substituting sodium diethyldithiocarbamate for potassium ethyl xanthate in the xanthate method. This method is called the "carbamate method." The next year, 1930, Kleinmann and Klinke (*13*) published another modification of the Biazzo method, and Cherbuliez and Ansbacher (*6*) proposed a titrimetric method by the use of nitrosochromotropic acid, called in this paper "chromotropic method."

During the last year some very promising reagents for the detection of copper have been suggested by Feigl and Kapulitzas (*9*, *10*), Kolthoff (*14*), and Sisley and David (*20*). Whereas Kolthoff states that by the use of *p*-dimethylaminobenzylidenerhodanine the amount of copper can be approximated, it is found that the color change is not sufficiently sensitive for quantitative work. Sisley and David's direct green B is very sensitive for the detection of copper, but the technic is not suitable for quantitative determinations.

More recently, new modifications of the xanthate and Biazzo methods have been proposed—i. e., those by Drabkin and Waggoner (*7*) and Gebhardt and Sommer (*11*). When one tries to recover known amounts of copper by either the xanthate or the Biazzo method difficulties and errors are encountered.

The xanthate method as developed by Supplee and Bellis is intended to be applied to the determination of copper in milk only. A sample of 15 grams of a drum process dried milk was analyzed following exactly the directions of Supplee and Bellis. The value obtained was 4.0 γ copper per gram ($1\gamma = 0.001$ mg.) for the combined filtrates from the ammonia precipitations. The second ammonia precipitate, after thorough washing, was dissolved, treated with hydrogen sulfide, and 0.2 γ per gram of copper recovered by the chromotropic method. The total amount of copper found was, therefore, 4.2 γ per gram, but when the entire analysis was made by the chromotropic method, only 1.5 γ per gram were recovered. That this latter value is correct is shown by the recovery of known amounts of copper added before destruction of the organic matter. Precipitation with ammonia is proposed by Supplee and Bellis to separate from iron without resorting to hydrogen sulfide, thinking that it is not possible to precipitate completely small amounts of copper from an acid solution with hydrogen sulfide. The results obtained by this method as modified by Drabkin and Waggoner are much lower, the most important reason being that by adding pyrophosphate the removal of iron by ammonia is made more quantitative. Iron interferes so markedly that about the same color was obtained with the xanthate from 50 γ of iron alone as from 12.3 γ of copper alone. Actually, hydrogen sulfide is considered in analytical chemistry to be the best means of separating metals of the second from those of the third group. In working with very small amounts of copper, the acid concentration must be more carefully controlled, and sulfur should be precipitated to adsorb and carry down the cupric sulfide. A few drops of nitric acid will produce sufficient sulfur to prevent a colloidal solution. That the copper sulfide precipitation is quantitative is also shown by Gebhardt and Sommer, who apparently even succeed in collecting it quantitatively by chloroform.

The reasons that the copper sulfide precipitation may sometimes not be quantitative are: (1) that the acid concentration is too high; (2) that the amount of sulfur precipitated is not sufficient to adsorb copper sulfide; (3) that the time allowed for settling is not sufficient; (4) that the use of paper filters is accompanied by losses; and (5) that the wash water used is not acid enough.

That the precipitation of copper with hydrogen sulfide can

[1] Received April 18, 1931.

be quantitative is shown in Table I, the copper being estimated by the chromotropic reagent.

Table I—Precipitation of Copper with Hydrogen Sulfide

Stand. Soln.	Total Vol.	Aliquot	Copper Calcd.	Copper Recovered	Difference	
Cc.	*Cc.*	*Cc.*	γ	γ	γ	%
10.00	100	10	49.1	49.5	+0.4	+0.8
1.00	10	10	49.1	49.2	+0.1	+0.2
0.25	5	5	12.25	12.1	−0.25	−1.2[a]

[a] Reagent only accurate to 0.5 γ of copper.

As to the match with potassium ethyl xanthate, the turbidity is so annoying that the color comparison must often be repeated to get constant values. The samples generally produce cloudiness more rapidly than the standard solutions so that accurate comparisons are often difficult. The match is more satisfactory for solutions containing about 100 to 200 γ of copper, but if less than 50 γ are present the values are apt to be sometimes more than 10 per cent too high.

The disadvantage that the solutions are cloudy with potassium ethyl xanthate is not removed by the carbamate method, but the results obtained with 10 to 50 γ of copper are much better than those by the xanthate method. This turbidity is undoubtedly due to the presence of other metals, Callan and Henderson having shown that such turbidities are produced with the carbamate reagent by a number of metals.

As to the Biazzo method proposed by Elvehjem and Lindow, at first an attempt was made to match standard copper solutions. The colors developed were not constant. When to each of two samples of 73.7 γ of copper (taken from a microburet containing a copper standard solution) 5 cc. of *N* hydrochloric acid, 4 cc. of water, 3 drops of phenolphthalein, enough normal sodium hydroxide to make the solution just alkaline, 1 cc. of glacial acetic acid, 1 cc. (10 per cent) of potassium thiocyanate solution, 10 drops of pyridine, and 2 cc. of chloroform (accurately measured) were added, the difference of the two readings was 13.5 per cent. By the same treatment, two solutions of 98.2 γ of copper differed by 28.6 per cent. Closer results were attempted by omitting the phenolphthalein. A sample of 98.2 γ of copper was compared with a sample of 110.5 γ of copper to each of which were added 3 drops of concentrated sulfuric acid, 1 cc. of (10 per cent) potassium sulfocyanate, 10 drops of pyridine, and 2 cc. of chloroform and an error found of 16.8 per cent. If 98.2 γ of copper were compared with 122.8 γ of copper, replacing the chloroform by 2 cc. of bromobenzene (b. p. 154° to 155° C.) as proposed by Kleinmann and Klinke, an error of only 1.3 per cent was found; in comparing 122.8 γ of copper with 147.3 γ of copper, 0.8 per cent; 147.3 γ of copper with 171.9 γ of copper, 4.8 per cent; and 171.9 γ of copper with 196.4 γ of copper, 5.6 per cent. Still better results were obtained by replacing the sulfuric acid by glacial acetic acid, and 49.1 γ of copper were matched against 98.2 γ of copper with 0.0 per cent error and 24.6 γ against 98.2 γ of copper with 0.4 per cent error. After this was observed it was noted that Gebhardt and Sommer, reporting the interference of phenolphthalein, have diminished the error by adding it as late as possible. The authors believe that phenolphthalein should not be used at all and it is omitted in the procedure developed later in this paper.

That the Biazzo method gives too low results is stated by Drabkin and Waggoner. But Schönheimer and Herkel (*17*) had already conceded that the higher results found with the chromotropic method by Andrianoff and Ansbacher (*1*) are right and that the low values found with the Biazzo method could not be repeated after new modifications (*12*).

As the result of experience in the determination of copper in human (*4*) and animal (*5*) organs and in foodstuffs (*15*, *16*), the following directions are offered.

Destruction of Organic Matter

Wet Digestion—A small sample is introduced into a Kjeldahl flask in which a funnel is placed to protect it against contamination. Moisten the sample with water, add about 15 cc. of concentrated sulfuric acid, and boil off the water until the residue becomes black and sulfur trioxide fumes are given off. Allow to cool and add not more than 5 cc. (20 per cent) of perchloric acid (the sulfuric acid concentration must be kept at least 50 per cent by volume), and 2 cc. of fuming nitric acid. Heat with a very small flame until no more nitrogen tetroxide fumes are given off, then increase the heat and continue until white fumes appear. Allow to cool, and if the solution is not colorless, start again with perchloric acid and nitric acid. The final volume is less than the amount of sulfuric acid used, sulfuric acid participating in the reaction.

Ashing in Electric Muffle—A large sample in a silica dish is placed on a hot plate until it is charred and then in an electric muffle at a temperature not exceeding 400° C. After 30 minutes take the dish out, allow to cool, add fuming nitric acid, and evaporate to dryness on a hot plate. Sometimes the oxidation is complete after this treatment. If only a small amount of organic matter remains, add more nitric acid and evaporate again to dryness. With larger amounts the dish must be replaced for 30 minutes in the muffle and after cooling nitric acid added again. Generally all the organic matter is completely oxidized by this treatment, but it can be repeated as often as necessary.

As to the destruction of organic matter, it is to be stated that wet digestion is undoubtedly trustworthy, and this procedure is not so tedious as that of the Association of Official Agricultural Chemists which was criticized by Walker (*23*). Furthermore, the dangers of both loss and contamination in ashing in open dishes are not to be underrated. As Gebhardt and Sommer found, ashing in the muffle is liable to give low values if the temperature of the muffle is too high. A much lower temperature was employed in the muffle than that indicated by these authors, but danger of contamination is hard to avoid.

Precipitation of Copper as Copper Sulfide and Its Re-Solution

The solution is carefully washed from the Kjeldahl flask into an Erlenmeyer, or if the sample was ashed in a silica dish, about 10 cc. of concentrated sulfuric acid are added, heated, cooled, water added, and the suspension washed into an Erlenmeyer. Dilute with water so that the acid concentration does not exceed 15 per cent by volume, heat to boiling, add a few drops of nitric acid, and allow a current of hydrogen sulfide to pass through the solution until it is cold, the Erlenmeyer being closed with a two-hole stopper. Let the precipitate settle, filter by suction through a small crucible with porous bottom (Central Scientific Co. No. 3810, fine) wash with water acidified by acetic acid and saturated with hydrogen sulfide until no more iron can be detected in the filtrate, place the crucible by means of a glass triangle over a small crystallizing dish which is on a glass water bath, and add fuming nitric acid to the crucible. When no more liquid remains in the crucible, wash it with water and allow it to remain on the water bath until evaporation of the solution containing copper nitrate and copper sulfate. Then place the crystallizing dish on a hot plate until no more acid fumes are given off. Care must be taken not to decompose the nitrate. Take up the residue with water.

This procedure has the following advantages: (1) no preliminary filtering from insoluble silicates, calcium sulfate, or lead sulfate; (2) complete separation from the metals of the third group; (3) separation from mercury salts; and (4) final neutral solution.

But care must be taken that the copper sulfide precipitate does not remain in contact with the air, and copper contamination must be excluded—i. e., by placing a glass plate over the crucible when filtering and dissolving. A very small amount of copper (a few micrograms) can be precipitated and recovered by this method.

Estimation of Copper

The neutral solution containing cupric ions is transferred to a volumetric glass-stoppered flask. If the color of copper sulfide precipitate in the crucible has been noted previously, it is easy after several analyses to estimate roughly the copper present. This approximation indicates the size of the flask which it is desirable to use.

Aliquots of the neutral solution are compared with a copper standard solution. About 2.5 grams of copper sulfate ($CuSO_4.5H_2O$) were dissolved in 250 cc. of water (25 cc. aliquot of this solution gave by electrolytic determination 0.0614 gram of copper). A 10-cc. aliquot was made up with water to 250 cc. This solution is called the copper standard solution and contains 49.1 γ of copper per cubic centimeter.

That all the reagents used for the estimation of copper must be examined for their possible copper content has been indicated by every investigator. The acids used here have been found to be sufficiently copper-free but the ordinary distilled water was found by the chromotropic method to contain 54.3 γ of copper per liter; tap water, 115.2 γ of copper per liter, and tap water distilled in a glass still, 18.4 γ of copper per liter. The ordinary distilled water, re-distilled in a glass apparatus, had to be used. No copper could be detected in this water with the method used.

Estimation of Copper with Xanthate Reagent—An aliquot of the neutral solution is pipetted into a Nessler tube to which 10 cc. (0.1 per cent) of potassium ethyl xanthate solution and water had previously been added. In a similar tube, place 10 cc. of the reagent and water, and let drop from a microburet the copper standard solution until the color is almost the same as that of the tube containing an aliquot of the sample. Make both up to the mark and add in one of the two tubes as many drops of the copper standard solution as are necessary to produce the same color. Then calculate the approximate amount of copper present in the sample and place 10 cc. of the reagent and water in each of six Nessler tubes, in the first of which let run as much copper standard solution as calculated, in the second 0.05 cc. less, in the third 0.1 cc. less, in the fourth 0.05 cc. more, in the fifth 0.1 cc. more, and in the sixth the same amount of the unknown as used before. Make up with water to the mark in the six tubes and match again. Most reliable results are obtained if from 100 to 200 γ of copper are present in the solutions compared.

Estimation of Copper with Biazzo Reagent—An aliquot of the neutral solution is pipetted into a 25-cc. separatory funnel. From a microburet run into another separatory funnel as much copper standard solution as corresponds approximately to the copper present in the sample, noting the color of the copper sulfide precipitate.

Add to each of the funnels about 10 cc. of water, 25 drops of glacial acetic acid, 30 drops of pyridine, 3 cc. (10 per cent) of potassium thiocyanate, and 2 cc. of bromobenzene (b. p. 154° to 155° C.). After thorough shaking, the bromobenzene is permitted to settle to the bottom of the funnels. Finally, draw off some of the bromobenzene from each funnel into the corresponding cups of the colorimeter. The amount of copper present in the bromobenzene layer should be between 50 and 150 γ for most satisfactory results.

Estimation of Copper with Carbamate Reagent—The directions are the same as indicated for estimation with the xanthate reagent, but replace the 10 cc. of xanthate reagent by 10 cc. (0.1 per cent) of carbamate reagent (sodium diethyldithiocarbamate).

Table II—Recovery of Added Copper in Food Materials

Sample	No.	Weight	Copper Added	Copper Recovered
		Grams	*γ/Gram*	*γ/Gram*
Skim milk	855	50 cc.	0	0.2
		50 cc.	137.5	137.5 + 0.2
Dryco	835	12.1	0	1.5
		12.8	98.2	98.2 + 1.5
Egg yolks	633	17.1	0	7.4
		6.0	98.2	98.2 + 7.1
Oysters	785	19.9	0	64.1
		5.0	98.2	98.2 + 64.3

Table III—Copper Estimation by Different Reagents

Reagent	Aliquot	Copper Calcd.	Copper Recovered	Difference	
	Cc.	γ	γ	γ	%
COPPER STANDARD SOLUTION, 10.00 CC.; TOTAL VOLUME, 50 CC.					
Xanthate	5	49.1	54.0	+4.9	+10.0
Xanthate	10	98.2	100.7	+2.5	+ 2.5
Biazzo	10	98.2	94.4	−3.8	− 3.9
Carbamate	5	49.1	48.4	−0.7	− 1.4
Chromotropic	5	49.1	49.1	0	0

		Copper Found Aliquot	Copper Found Sample
		γ	*P. p. m.*
DRIED SPINACH, 110 GRAMS; TOTAL VOLUME, 25 CC.			
Xanthate	5	246.4	11.2
Biazzo	2	88.9	10.1
Carbamate	1	46.6	10.6
Chromotropic	1	47.1	10.7
DRIED TOMATOES,[a] 21 GRAMS; TOTAL VOLUME, 25 CC.			
Xanthate	5	81.5	19.4
Biazzo	2	30.6	18.2
Carbamate	2	31.8	18.9
Chromotropic	2	31.3	18.7
TOMATOES,[b] 8 GRAMS; TOTAL VOLUME, 25 CC.			
Xanthate	9	56.4	19.6
Biazzo	5	27.4	17.1
Carbamate	6	34.6	18.0
Chromotropic	4	23.2	18.1

[a] Ashed in muffle.
[b] Wet digestion.

Table IV—Copper Determination with Chromotropic Reagent

Sample	No.	Weight	Copper Recovered	Copper Recovered Biazzo
		Grams	*P. p. m.*	*P. p. m.*
Klim	820	14.8	1.2	0.8[a]
Egg yolk	633	17.1	7.4	5.9– 6.1[a]
Lettuce	671	11.3	11.2	10.4–10.6[a]
Spinach	708B	5.6[a]	24.7[a]	19.1–20.5[a]
		15.3[a]	24.3[a]	
Oysters	785	19.9	64.1	58.4–59.6[a]
Klim	840	13.9	1.5	
Klim	846	21	1.8	
Klim	843	22	2.0	
Appleskin		84.3	3.0	
Apples	832	13.5	9.8	
Apples	833	14.0	12.4	

[a] Elvehjem and Lindow's modification of Biazzo method.

Estimation of Copper with Chromotropic Reagent—An aliquot of the neutral solution is pipetted into a test tube and 3 drops of ammonia added. Let drop from a buret the chromotropic reagent until the end point is reached. The number of cubic centimeters used, multiplied by the titer, gives the amount of copper present in micrograms.

An outline of the preparation of the chromotropic reagent and of the determination of its titer follows.

Preparation of Chromotropic Reagent—The cupric ions in ammonia solutions, with some *o*-nitrosohydroxyl aromatic derivatives, form lakes of very intense color, which is different from that of the organic derivative. For example, the 1,8-dihydroxy-2-nitroso-3,6-naphthalenedisulfonic acid (usually called nitrosochromotropic acid) forms with copper, in weakly ammoniacal solution, a compound which has a very intense permanganate color resulting from the union of one cupric ion with two molecules of the nitrosochromotropic salt. As soon as an excess of the yellowish brown nitroso dye is present, the permanganate color changes to brown. This color change serves as indicator and it is possible to titrate very small amounts of copper with an accuracy of 0.5 γ.

Dissolve 0.37 gram (0.001 mol) of the sodium salt of the chromotropic acid in a small amount of water, add 1 cc. of 2 *N*

sodium carbonate and 0.5 to 0.6 cc. of 2 N sodium nitrite, and a small excess of dilute acetic acid. After 24 hours, filter, make weakly alkaline with sodium carbonate, dilute with water to 100 cc. (0.01 N), take out 34 cc., and dilute with water and 50 cc. of alcohol to 1 liter. This solution is called the "chromotropic reagent," 1 cc. of which corresponds to about 10 γ of copper.

Standardization of Chromotropic Reagent—For the determination of the titer of the reagent, let drop from a microburet 1.00 cc. (49.1 γ of copper) of the copper standard solution into a test tube, add 3 drops of concentrated ammonia, follow with the reagent, dropping from a buret while shaking the test tube. The first drops give the permanganate color mentioned above. When all the cupric ions are combined, this color changes to brown. To recognize the end point, titrate in a very good daylight, school the eyes to the color change, and compare with two solutions, of which one has not yet reached the end point and the other has just passed it. As the end point is approached, add only parts of a drop of the reagent to obtain a maximum of precision. If 1 cc. of the copper standard solution required 7.32 cc. of the reagent, its titer is

$$\frac{49.1}{7.32} = 6.7\ \gamma \text{ of copper}$$

Known amounts of copper were added before the destruction of the organic matter to fresh skim milk, dried milk, egg yolks, and oysters, and the recovery values, obtained by the chromotropic reagent and shown in Table II, prove that the procedure employed is reliable. Recoveries were exact within the limits of estimation (0.5 γ).

To compare the different reagents, the analyses in Table III were made.

The values given in Table IV were obtained with the chromotropic reagent, some, as indicated, by Elvehjem and Lindow's modification of the Biazzo method.

Literature Cited

(1) Andrianoff and Ansbacher, *Deut. med. Wochschr.*, **56**, 357 (1930).
(2) Biazzo, *Ann. chim. applicata*, **16**, 2 (1926).
(3) Callan and Henderson, *Analyst*, **54**, 650 (1929).
(4) Cherbuliez and Ansbacher, *Arch. path. Anat.*, **278**, 365 (1930).
(5) Cherbuliez and Ansbacher, *Arch. Sciences Genève*, **5**, ii, suppl. 144 (1929).
(6) Cherbuliez and Ansbacher, *Helv. Chim. Acta*, **13**, 187 (1930).
(7) Drabkin and Waggoner, *J. Biol. Chem.*, **89**, 51 (1930).
(8) Elvehjem and Lindow, *Ibid.*, **81**, 435 (1929).
(9) Feigl, "Qualitative Analyse, mit Hilfe von Tüpfelreaktionen," p. 154, Akademische Verlagsgesellschaft, 1931.
(10) Feigl and Kapulitzas, *Mikrochemie*, **8**, 239 (1930).
(11) Gebhardt and Sommer, Ind. Eng. Chem., Anal. Ed., **3**, 24 (1931).
(12) Herkel, *Beitr. path. Anat.*, **85**, 514 (1930).
(13) Kleinmann and Klinke, *Arch. path. Anat.*, **275**, 422 (1930).
(14) Kolthoff, *J. Am. Chem. Soc.*, **52**, 2222 (1930).
(15) Remington, *Southern Med. J.*, **24**, 52 (1931).
(16) Remington and Shiver, *J. Assocn. Official Agr. Chem.*, **13**, 129 (1930).
(17) Schönheimer and Herkel, *Klin. Wochschr.*, **9**, 1449 (1930).
(18) Schönheimer and Oshima, *Z. physiol. Chem.*, **180**, 249 (1929).
(19) Scott, "Standard Methods of Chemical Analysis," p. 165, Van Nostrand, 1918.
(20) Sisley and David, *Bull. soc. chim.*, [4] **47**, 1188 (1930).
(21) Spacu, *Analyst*, **49**, 275 (1924).
(22) Supplee and Bellis, *J. Dairy Sci.*, **5**, 455 (1922).
(23) Walker, *J. Assocn. Official Agr. Chem.*, **13**, 426 (1930).

Estimation of Solids in Steam by Conductivity[1]

J. K. Rummel

The Babcock & Wilcox Co., Bayonne, N. J.

Improvements to and applications of an electrical conductivity method of estimating solids in steam are discussed from the viewpoint of investigating and inhibiting objectionable deposits on steam-contact surfaces.

A gas separator has been developed for removing objectionable gases, principally carbon dioxide, from steam samples, thereby refining the method and avoiding large corrections to readings.

The importance of producing steam free from solids which will cause deposits on steam-contact surfaces, is of considerable importance to both operators and manufacturers of steam-generating equipment. In power-generating stations, solids have deposited on superheaters, turbines, and other parts, causing serious losses in operating efficiency. These deposits have taken forms which vary in composition from water-soluble salts, which can be removed by washing with water or saturated steam, to hard silica scale, which resists all practical solvents and must be removed by hand. Hard silicate or silica deposits have been especially troublesome.

Owing to the various conditions under which deposits have formed, all the factors governing their formation are most difficult to define, and to date it has been necessary to study many cases separately. In general, the kind and amount of solids in the steam is the most important consideration. The amount of solids will vary with certain boiler-water concentrations, rates of evaporation, water level, and the design of the evaporating and steam-separating equipment. By changing one or more of these factors, particularly the concentrations of objectionable solids in the boiler water and the steam-separating equipment within the boiler, these troubles have been stopped or reduced to a marked extent.

In the study of this problem, it has been necessary to develop a sensitive method of estimating the amount of solids carried in the steam. The first work by the author, in 1926, employed a method of evaporating 20-liter samples of steam condensate and weighing the residue. Considerable error was introduced by the solubility of the glass sample bottles and possibly from dust in the air and, in general, the results were not conclusive. In 1927, in coöperation with others, an electrical conductivity method of estimating steam quality was developed and later reported by Fitze (*3*). In following years, more details and applications were added, particularly in coöperation with the Commonwealth Edison Company (*1*) and by the independent work of Hecht and McKinney (*4*). To compare results with the standard steam calorimeter method, the results of these tests were all reported in terms of per cent moisture, Hecht and McKinney using the expression "entrainment." Since the electrical conductivity readings vary with the dissolved solids and not with the per cent moisture, like the steam colorimeter readings, it is recommended that the electrical conductivity method be the standard for estimating solids, and the results be expressed as parts per million of solids instead of per cent moisture or equivalent boiler water. This conductivity method is particularly valuable in the estimation of small amounts of solids which might be detected only with difficulty by the calorimeter.

As indicated by Washburn (*5*), one of the chief difficulties in obtaining accurate results by the electrical conductivity procedure is in the application of suitable corrections for dissolved carbon dioxide gas. In dilute solutions, the presence of carbon dioxide not only influences the conductivity readings to a marked extent, but its effect on other solids in the sample makes an exact correction difficult. Thus, con-

[1] Received March 25, 1931.

sidering the small amounts of solids carried in the steam from many modern boilers, and the considerable amounts of carbon dioxide which are often present, it is proposed to use a gas separator and steam condenser instead of the conventional closed condenser and cooling coil, both shown in Figure 1. Then, having removed all but a very small determined amount of objectionable carbon dioxide, a more accurate correction may be made. As summarized by Creighton (*2*), and as found by experience with the method employed, the conductivity of pure water is so small as to be almost insignificant. Therefore, large water corrections, based on an assumed carbon dioxide content, are to be discouraged.

Gas Separator and Steam Condenser

In Figure 1, which illustrates the equipment used for the electrical conductivity test, the item of principal interest is a recently designed gas separator and steam condenser, the principal parts of which are described as follows:

1—The preliminary condenser, connected to the steam-sample line and the top of the gas-separating chamber, is made of a short length of copper tube 6 mm. in diameter inside of a tubular jacket, which is wound around the top of the separator chamber. The smaller tube carries the steam sample while cooling water is connected to the jacket.

2—The gas-separator chamber consists of a copper shell approximately 10 cm. in diameter by 40 cm. long, with brass heads top and bottom. Brass petcocks are placed in the side of the shell to indicate water level. The top head contains the sample inlet and the gas and steam outlet which may have a steam condenser connected to it. The bottom head contains water-inlet and -outlet chambers to which are connected three cooling coil sections of copper tubing 6 mm. in diameter, occupying the bottom part of the chamber, also, the steam-condensate outlet and drain connections.

3—The final cooling coil, connected to the bottom head of the separating chamber, is wound around the bottom part of the chamber and is constructed in the same manner as the preliminary condenser at the top of the chamber.

4—The conductivity cell, at the side of the separator shell, is connected with the outlet of the final cooling coil and is constructed of either glass or copper. Its approximate dimensions are 37 mm. in diameter by 150 mm. long, and it is equipped with a Leeds & Northrup dip cell and thermometer, which are held in place by a rubber stopper in the top. The steam condensate enters by the bottom connection and leaves by the top.

5—Among the accessories, attention is called to the compression fittings used to make connections with the copper tubing. These are particularly useful in making the jacketed cooling coils.

The steam flow to the apparatus and the water to the preliminary condenser are regulated by needle valves. The water to the various cooling coils is regulated by ordinary brass globe valves.

The steam and gas outlet, or vent, on the top of the separator chamber, has, in former designs, been fitted with a condenser from which the steam being vented could be measured. This may be added if desired, but is not essential.

The original gas separator and condenser which was used in most of the experiments to date was of larger proportions, and no doubt this and the apparatus shown may be varied in design to improve efficiency and ease of control. Figure 1, therefore, may be considered as schematic.

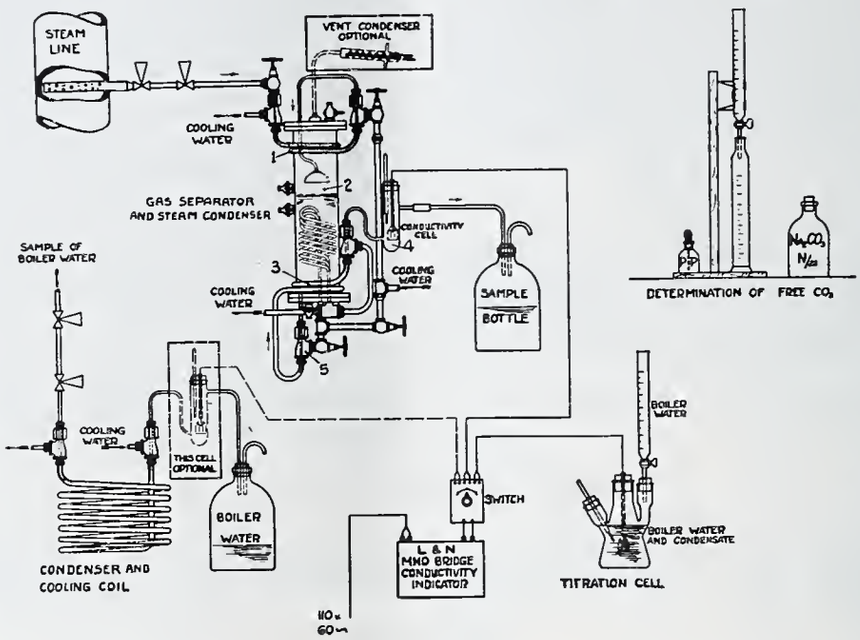


Figure 1—Assembly of Conductivity Testing Equipment

The balance of the equipment is conventional to the electrical conductivity method and is largely self-explanatory. The Leeds & Northrup bridge reads in terms of conductivity and the dip cell has a constant of approximately 0.1.

Method of Operation

In the operation of the gas separator and condenser, the flow of steam from the sample pipe is regulated by the throttle valve to pass approximately 500 ml. or less of steam-condensate equivalent per minute, and the cooling-water valve for the preliminary condenser is opened to condense a part of the steam. Simultaneously, the cooling-water valves for the internal cooling coils and the final cooling coil are opened to give approximately a full flow of water. The steam entering the separator chamber is then condensed, and the condensate level in the separator is automatically raised until it is above the top of the internal cooling coils and flows out from the bottom through the final cooling coil and the conductivity cell. The next step is the regulation of the cooling water to the cooling coils and preliminary condenser, and the flow of steam to the apparatus. Thus, a proper balance will be maintained to vent only a little steam from the gas and steam outlet and deliver condensate to the conductivity cell, which will have a temperature of approximately 25° C. (77° F.) and contain not much in excess of one p. p. m. of free carbon dioxide, as shown by the test illustrated in Figure 1. The greatest difficulty so far encountered is regulating the flow of steam sample and cooling water to the preliminary condenser. With a layer of boiling water over the internal cooling coils, the cooling water to these, and the final cooling coil, will require relatively little attention. The valve on the steam-sample line ahead of the needle valve may be used as a pressure regulator, and by throttling on this and the needle valve simultaneously, a more constant flow of steam may be obtained. A pressure-regulating valve could be used for the same purpose.

When these conditions have been obtained, one can proceed with the conductivity measurements of the condensate and the collection of a continuous sample of boiler water, all of which are used to calculate the solids in the steam.

Evaluation and Interpretation of Results

Briefly, the adopted conductivity procedure consists of obtaining simultaneous samples of steam condensate (having a minimum of carbon dioxide) and boiler water, both of which are cooled to approximately 25° C., from which the following data are obtained: conductivity of steam condensate, conductivity of 1 per cent solution of boiler water in steam-condensate sample, temperature of these samples, and the solids in the boiler water.

From these data the parts per million of solids in the steam may be calculated by the following formula:

$$\text{P. p. m. of solids} = \frac{Ls - Wc}{S \times 100} \times \text{p. p. m. solids in boiler water}$$

where Ls = conductivity of steam condensate at standard temperature
Wc = total conductivity correction due to carbon dioxide and pure water
S = conductivity increase due to adding 1 per cent boiler water to steam condensate, result corrected to standard temperature

Note—The p. p. m. of solids in the steam may be either the total solids or the soluble solids, depending on which is included in the boiler-water sample which is taken for evaporation. The conductivity measurement includes only the soluble ionized solids in the sample. The S value in the formula is preferred to one in which S equals 100 per cent boiler water, the reason being that it is more desirable to have readings in the same dilution range and subject to the same variations as the steam-condensate sample.

The work of determining solids in the boiler water by evaporation may be minimized by plotting total solids against conductivity for a given boiler water and estimating solids from the conductivity values.

Table I—Conductivity-Temperature Corrections to 77° F. (25° C.)
(Conductivity reading × K value = corrected conductivity)

Temperature ° F.	K Value	Temperature ° F.	K Value
60.0	1.2615	80.5	0.9591
60.5	1.2519	81.0	0.9535
61.0	1.2423	81.5	0.9480
61.5	1.2331	82.0	0.9425
62.0	1.2238	82.5	0.9371
62.5	1.2148	83.0	0.9318
63.0	1.2058	83.5	0.9265
63.5	1.1971	84.0	0.9213
64.0	1.1883	84.5	0.9162
64.5	1.1799	85.0	0.9110
65.0	1.1713	85.5	0.9061
65.5	1.1631	86.0	0.9011
66.0	1.1550	86.5	0.8962
66.5	1.1468	87.0	0.8913
67.0	1.1389	87.5	0.8865
67.5	1.1310	88.0	0.8817
68.0	1.1233	88.5	0.8770
68.5	1.1156	89.0	0.8726
69.0	1.1082	89.5	0.8677
69.5	1.1007	90.0	0.8632
70.0	1.0933	90.5	0.8586
70.5	1.0861	91.0	0.8542
71.0	1.0790	91.5	0.8497
71.5	1.0719	92.0	0.8454
72.0	1.0650	92.5	0.8410
72.5	1.0581	93.0	0.8367
73.0	1.0513	93.5	0.8325
73.5	1.0446	94.0	0.8282
74.0	1.0380	94.5	0.8241
74.5	1.0314	95.0	0.8200
75.0	1.0250	95.5	0.8159
75.5	1.0186	96.0	0.8119
76.0	1.0124	96.5	0.8079
76.5	1.0061	97.0	0.8039
77.0	1.0000	97.5	0.8000
77.5	0.9939	98.0	0.7961
78.0	0.9879	98.5	0.7923
78.5	0.9820	99.0	0.7884
79.0	0.9762	99.5	0.7847
79.5	0.9704	100.0	0.7809
80.0	0.9647		

In making comparisons with the steam calorimeter and expressing results in terms of equivalent moisture in the steam, the following formula may be used:

$$\% \text{ equivalent moisture} = \frac{Ls - Wc}{S}$$

Dealing with corrections to the data obtained and the estimation of the Wc value, the following is of interest:

Since more than one conductivity cell may be used in this work, it is customary to determine cell constants with a 0.02 N potassium chloride solution and express results in terms of specific conductivity. The conductivity reading times the cell constant equals specific conductivity. The formula used for determining the cell constant is:

$$C = \frac{L}{Ls}$$

where C = cell constant
L = specific conductivity of KCl solution
Ls = measured conductivity of KCl solution when using unknown cell

Since it is not practical to make all the readings at the standard temperature of 25° C. (77° F.) and degrees Fahrenheit are standard for power-plant work, the temperature is read and the results corrected by the following formula:

$$Ls = Lm\left(\frac{Ts + 5}{Tm + 5}\right), \text{ or } Ls = Lm \times K$$

where Ls = conductivity at standard temperature
Lm = measured conductivity
Tm = measured temperature, ° F.
Ts = standard temperature, ° F.

$$K = \frac{Ts + 5}{Tm + 5}$$

Table I gives values of K for temperatures from 60° to 100° F.

Water and carbon dioxide corrections are the most difficult to determine with accuracy. For example, it is not definitely known how much the sample is contaminated by the sampling equipment or the maximum effect of free carbon dioxide on the alkalies and other dissolved solids in the sample. Figure 2 gives the average of several hundred determinations of the carbon dioxide effect in samples of distilled water. The carbon dioxide was determined for 100-ml. samples by the method illustrated in Figure 1. The water used had a specific conductivity of 1×10^{-6} mho, having been freed of carbon dioxide by boiling and bubbling nitrogen gas through it at the same time. Carbon dioxide was then added from a cylinder and by progressive determinations and dilutions the various points on the curve of Figure 2 were determined. This curve will give an approximate correction for carbon dioxide as determined in the steam-condensate sample.

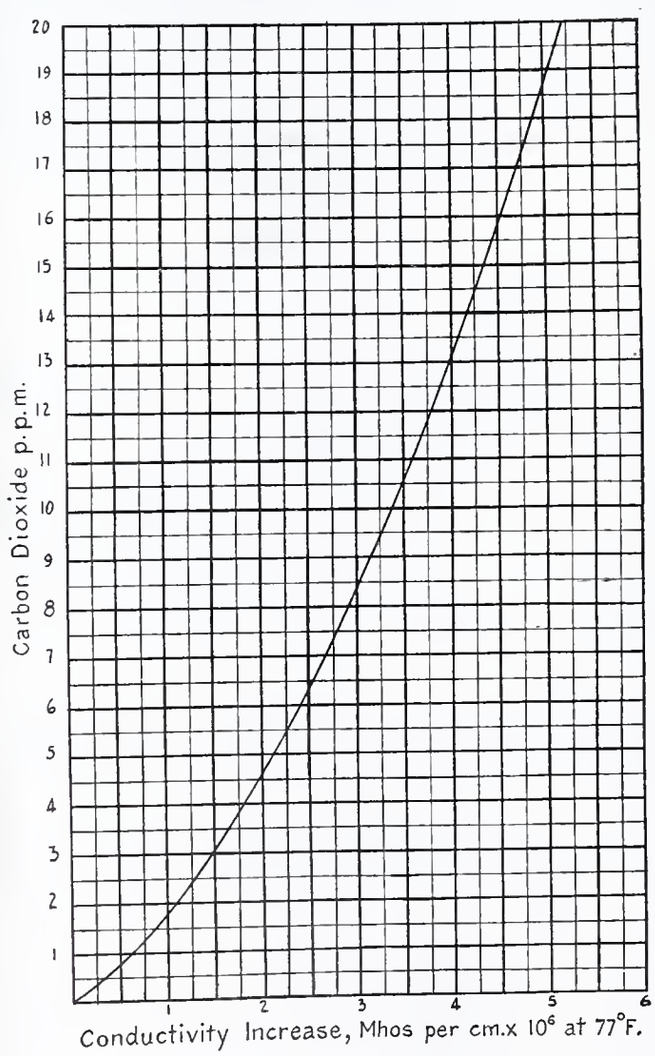


Figure 2—Effect of Carbon Dioxide Content on Conductivity of Steam Condensate

Assuming that the sampling equipment does not contaminate the sample to any marked extent, a correction for pure water of 0.1×10^{-6} mho specific conductivity should be

sufficient. Some assurance is given to this assumption by actual steam-condensate readings from Stirling boilers in the order of 0.5×10^{-6} mho, with no correction for carbon dioxide. The previously suggested correction of 0.9×10^{-6} mho is therefore believed to be too high.

Having made the above corrections and obtained a value for solids in the steam under different operating conditions, one may arrive at some conclusions as to the best practical method of operation to give the lowest solids and theoretically the least amount of trouble from deposits. However, the total amount of solids found is not an infallible guide to the quantity or rate of deposit formation and the type of equipment and the use to which the steam is put must be considered. Previous experience and results will also be of material aid in reaching reasonable conclusions. The analysis of the boiler water is often a guide to the probability of deposit formation, and after some experience with a certain system, it is possible to set certain limits of boiler-water concentrations below which trouble may be avoided. For example, limits placed on the silica or other solids in the boiler water have been found to be effective. In addition to the above, the conductivity method is often useful in comparing the solids in the steam from different boilers or other apparatus, such as evaporators, and trace the source of the largest amounts of solids.

For certain practical purposes, it is not always necessary to go through the entire procedure as far as the calculation of solids. That is, the results in terms of specific conductivity of the steam condensate will indicate whether a large or small amount of solids is present, particularly when the carbon dioxide has been largely removed by use of the gas separator and condenser. However, to develop the art and obtain records which will be useful for a complete study of deposit formation, the general practice should be to obtain complete information.

It is concluded that despite some evident sources of error in the methods which must be used in practical work, the conductivity method of estimating solids or equivalent moisture in steam condensate will be a valuable aid in the study of power-plant and related problems. Similar electrical conductivity methods of estimating condenser leakage and boiler water solids have enjoyed considerable popularity and success.

Acknowledgment

Acknowledgment is made to the personnel of the Research Development Department of the Babcock & Wilcox Company and others for helpful suggestions in developing the method.

Literature Cited

(1) Commonwealth Edison Co., *N. E. L. A. Publication*, No. 051, 14–9 (June, 1930).
(2) Creighton and Fink, "Electro-Chemistry," Vol. I, pp. 89–91, 2nd ed., Wiley.
(3) Fitze, *Power*, **68**, 484–5 (1928).
(4) Hecht and McKinney, "Electrical-Conductance Measurements of Water and Steam," paper presented before Am. Soc. Mech. Eng., June, 1930.
(5) Washburn, *J. Am. Chem. Soc.*, **40**, 89–91 (1918).

An Extractor for Biological Products[1]

Chas. L. Shrewsbury

PURDUE UNIVERSITY AGRICULTURAL EXPERIMENT STATION, LAFAYETTE, IND.

THE extraction of large amounts of materials for use in nutrition investigations becomes a problem with the apparatus that can be fabricated or purchased.

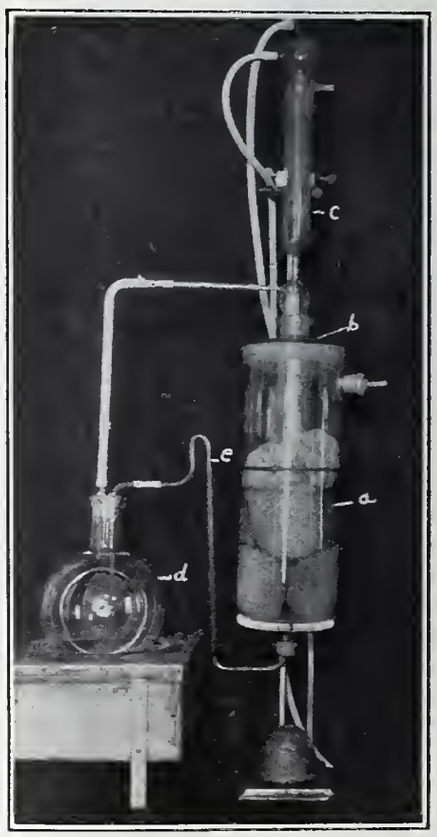
Guerrant (*1*) described an extractor that can be assembled in most laboratories. Experience has demonstrated that considerable quantities of vapor escape through the seal between the bell jar and desiccator top in this type of extractor. In addition, one must use a liberal application of sealing compound at this joint which may contaminate the solvent and which is objectional when the extract is to be incorporated in feeds.

The extractor illustrated in the photograph is one that was designed with the view of eliminating the above objections. The extraction chamber, *a*, is molded of medium-weight glass that will withstand rapid temperature changes and moderate negative pressure. It is fitted with a ground glass top, *b*, which is provided with a ground glass opening to receive a condenser, *c*. The condenser is constructed so that vapors are led directly into the extraction chamber, providing for a hot extraction of the material. If the cold extraction process is used, the vapors are led in through the top of the condenser.

The ground glass condenser and top joints require little or no sealing compound to effect a tight seal. When operating without sealing compound, no difficulty has been experienced with the top becoming fast or with loss of solvent.

The solvent is placed in a 5-liter round-bottom Pyrex flask, *d*, and heated on the steam bath. The condensed vapors and extractives are returned to the boiling flask by means of the siphon tube, *e*. The operation of the extractor is continuous and automatic.

The extractor has a capacity of approximately 5 liters and will hold from 3 to 5 kg. of feeding stuffs.



An Extractor for Biological Products

Literature Cited

(1) Guerrant, N. B., IND. ENG. CHEM., **18**, 1090 (1926).

[1]Received March 12, 1931.

Potentiometric Titration in Non-Aqueous Solutions

I—Differential Method for Determining Oil Acidity[1]

Beverly L. Clarke, Leland A. Wooten, and K. G. Compton

Bell Telephone Laboratories, Inc., 463 West St., New York, N. Y.

THE increasing importance of the accurate determination of the acid number on lubricating and insulating oils, as well as on a variety of other materials, such as asphalts and nitrocellulose products, which are insoluble in water, has occasioned a number of attempts to devise satisfactory methods. None of these has been completely successful. The several proposed variations (*2*, *4*) of the colorimetric method have had a limited applicability to oils giving a nearly colorless solution. Kremann and Schöpfer (*6*) made an early attempt to apply electrometric principles to the problem, dissolving their fats or fatty acids in ethyl alcohol and using a cell consisting of a calomel reference electrode joined through a sodium chloride bridge to an electrode comprising a piece of bright platinum dipping into the unknown solution and flooded with a stream of nitrogen or air. Another method (*1*) uses as solvent a benzene-alcohol mixture containing potassium iodide, and instead of the usual calomel half-cell, employs a beaker of the neutralized solvent electrically bridged to the unknown solution. The end point is taken as corresponding to a zero e.m.f. between two bright platinum wires of which one is immersed in each solution.

Seltz and McKinney (*7*) suggested for the potentiometric titration of oil acidity a method using amyl alcohol saturated with lithium chloride as a solvent and also as the reference electrode, quinhydrone being added to both half-cells. Bright platinum electrodes were used. In a subsequent paper (*8*) amyl alcohol was abandoned in favor of butyl alcohol, also saturated, however, with lithium chloride, and in place of the cumbersome reference half-cell first used, a silver–silver chloride electrode was specified. Although this method seemed to be the most satisfactory that had been recommended, the troublesome technic suggested for preparing the reference electrode and its short life, together with the failure of the authors to specify necessary details concerning the preparation and care of the alcoholic caustic solution used as reagent, seemed to reduce the usefulness of the procedure for routine purposes. It was also discovered that the preliminary saturation of the butyl alcohol with lithium chloride greatly reduced its solvent powers for oils and produced such a viscous mixture that thorough mixing during the course of a titration was difficult and slow, resulting in drifting, uncertain potential differences.

It will be clear from the foregoing that the several potentiometric methods proposed for oil-acidity measurement differ essentially in the solvent, the nature of the reference electrode, and the presence or absence of an accessory substance like quinhydrone. In a systematic effort to effect improvements in these directions, we have perfected a method which, while comprising no radical departures from standard potentiometric practice, nevertheless can be presented in a refinement of manipulative detail which was absent in the other published methods examined. Although the butyl alcohol recommended by Seltz and Silverman (*8*) has been adopted as the oil solvent, it has been found necessary to make elaborate specification of detail concerning the storage and use of this solvent, and the drastic reduction in the lithium chloride concentration, for the reasons given in the preceding paragraph, increased the resistance of the electrode system so that ordinary instruments became rather insensitive. This has made necessary the adaptation of an electrical measuring instrument, the thermionic titrometer, so that it will permit a direct reading of the differential of the titration curve in systems having a high resistance. This instrument, which will have a wide usefulness in a laboratory doing potentiometric work, may be economically constructed and requires no special skill for its operation. The method here proposed shares with other potentiometric methods the advantage that opaque as well as colorless oils may be titrated.

[1] Received April 15, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Description and Use of Apparatus

The apparatus employed consists of a thermionic titrometer (*5*), an electrode system, a titration cell, and a reservoir for storage of the alkali. Since the success of the method depends to a large extent upon the quality and characteristics of the apparatus, a rather detailed description will be given.

Thermionic Titrometer—The thermionic titrometer is an instrument designed to give the differential titration curve directly. It combines ease of operation with such high sensitivity that it will operate satisfactorily with solutions having electrical resistances as high as 100 megohms (about 10 times the specific resistance of ethyl alcohol or benzene).

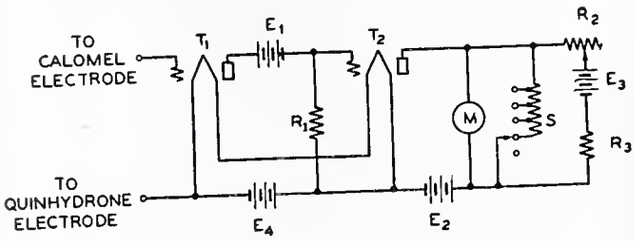


Figure 1—Diagram of Apparatus

T_1—Western Electric 102-G vacuum tube
T_2—Western Electric 101-D vacuum tube
E_1—135-volt battery
E_2—135-volt battery
E_3—18-volt battery
E_4—6-volt battery, lead accumulator
R_1—15,000-ohm fixed resistor
R_2—0 to 10,000-ohm variable resistor
R_3—1000-ohm fixed resistor
S —Shunt for meters, adjustable so that full-scale deflections correspond to currents of 0.1, 1, 10, and 100 milliamperes, respectively
M—Direct current milliammeter

Essentially, the instrument, which is an improvement on that originally developed by one of the authors (*5*), consists of a vacuum tube circuit so arranged that any change in the potential of an indicator electrode upon the addition of an increment of reagent causes a large deflection of an indicating meter. The schematic diagram in Figure 1 shows how this is accomplished.

The electromotive force of the cell to be measured is impressed upon the grid of the 102-G tube, T_1. An increase or decrease in the voltage of this cell will cause a change in the current flowing through the resistor R_1, and therefore a change in the potential of the grid of the 101-D tube. Owing to the amplifying power of the 102-G tube, this second grid potential change is much greater than that of the first tube. Consequently, a much greater change of plate current will occur in the second tube, and will be indicated by the meter M.

Experience in this laboratory has indicated that the Western

Electric 102-G and 101-D vacuum tubes are the most satisfactory of any commercially available for purposes of this nature. The tubes are very steady and constant in their characteristics, and have good saturation, so that they may be operated on 80 per cent of rated filament current without materially altering their characteristics. Our experience has indicated that the high insulation of the grid of the 102-G tube makes it more suitable than the shielded grid tubes for measurements in fairly high resistance systems.

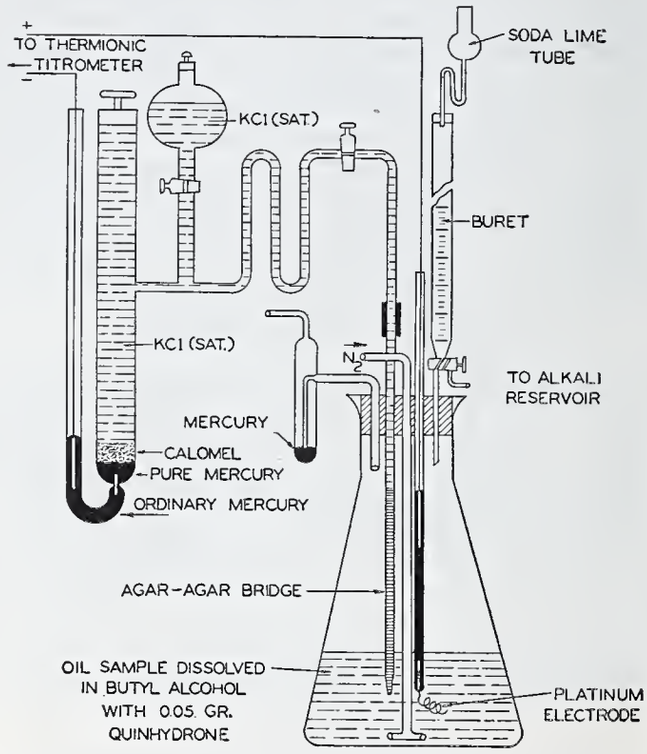


Figure 2—Assembled Cell

All resistors, tap switches, and connections in the instrument are well made so that no erratic changes take place in the circuit constants. As far as possible, all connections are soldered. The number of variable controls has been reduced to the shunt on the meter and the adjustment for setting the meter needle to zero, thus simplifying the operation of the circuit.

To prepare the instrument for a titration the meter, M, is short-circuited by means of one of the shunts at S, and the various batteries connected. The electrodes are then placed in the circuit and R_2 adjusted until the meter reads zero on the most sensitive scale. In case erratic fluctuations of the meter needle are encountered, it is necessary to short-circuit the meter, disconnect the electrodes, and connect the terminals of the instrument together. If the trouble disappears when the meter is again set at zero on the most sensitive scale, the trouble is in the electrodes. If the trouble remains, it is due either to faulty connections in some part of the circuit, or to faulty batteries. The batteries should be replaced with new ones, and the circuit traced for possible bad contacts.

There are certain important precautions to be exercised in the use of the titrometer. Whenever the electrodes are removed from the solution or disconnected from the instrument, the meter should first be short-circuited to prevent its being damaged. Furthermore, the meter should not be set on the most sensitive scale while an increment of reagent is being added to the solution in the titration cell. Old and badly used batteries and those having a low capacity should not be used, as they will tend to cause drifts or erratic fluctuations of the meter needle. If the instrument is in daily routine use, the batteries should be left permanently connected to avoid delays while waiting for the circuit to reach a steady state. The curvature of the voltage-meter deflection curve is so slight, and the portion actually used for the graphical estimation of the end point so small, that this curve may be considered a straight line.

Electrode System—The reference electrode was a saturated calomel half-cell, which made contact with the solution through an agar-agar salt bridge. The agar-agar mixture (7) was added while hot to a tube 15 cm. by 6 mm. in diameter, one end of which was drawn out to a capillary, until the tube was about one-half full. The remainder of the tube was filled with saturated potassium chloride solution. The assembled half-cell is shown in Figure 2. While it was necessary occasionally to replace the agar-agar bridge, the same half-cell was used for a period of more than twelve months.

The indicator electrode consisted of a bright platinum wire dipping into the non-aqueous solution to be examined, to which quinhydrone had been added. The platinum wire was cleaned after use by heating in the oxidizing tip of a Bunsen flame. All titrations were carried out in an atmosphere of nitrogen, which served both to stir the solution and to exclude carbon dioxide.

Reagents—A solution of potassium hydroxide in butyl alcohol (0.05 N) was used as a standard reagent in all titrations. The alcohol used for this purpose was freed from aldehyde by treatment with silver nitrate in alkaline solution. Water was removed by refluxing with quicklime followed by distillation in an atmosphere of nitrogen. The potassium hydroxide was of c. p. quality prepared by crystallization from alcohol. After preparation the solution was stored in a Pyrex bottle made light-proof by painting with black lacquer and protected from atmospheric contamination by towers of

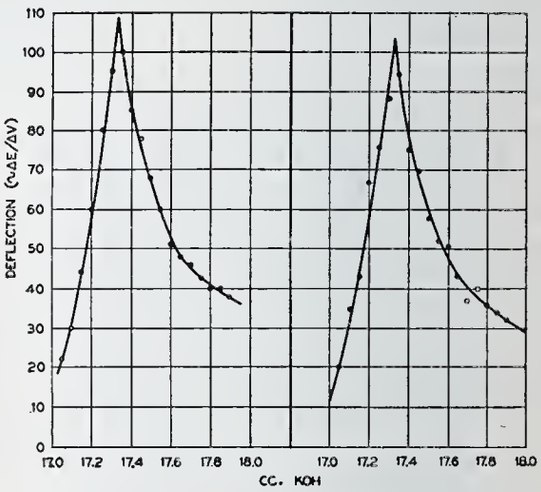


Figure 3—Titrations of Benzoic Acid Dissolved in Butyl Alcohol

soda lime and alkaline pyrogallol. The buret was connected to the alcoholic solution by means of a siphon so that the solution was never exposed to oxygen or carbon dioxide. This solution was standardized by titration against 100-mg. portions of Bureau of Standards' benzoic acid dissolved in the prescribed solvent. The standard alkali solution prepared and stored in this way was found not to vary appreciably in strength over a period of ten weeks.

The solvent used for oils and fats was n-butyl alcohol. A saturated solution of lithium chloride in butyl alcohol was prepared by adding an excess of the salt to a portion of the alcohol and refluxing for several hours. The saturated solution was stored in a Pyrex bottle made light-proof as described.

The quinhydrone used in all titrations was obtained from the Eastman Kodak Company.

Recommended Procedure

Dilute 10 cc. of the saturated lithium chloride–butyl alcohol mixture to 110 cc. with the pure solvent and dissolve in it approximately 50 mg. of quinhydrone. Add this solution to a 250-cc. wide-mouthed Erlenmeyer flask containing approximately 10 grams of the oil sample. Shake until solution is complete. Carry out the titration as follows:

Place titration cell in position (Figure 2) and allow a stream of nitrogen to bubble through the solution for 10 minutes before starting titration. By means of the two-way stopcock fill the buret with standard alkali. Connect electrodes to titrometer, as shown in Figure 1.

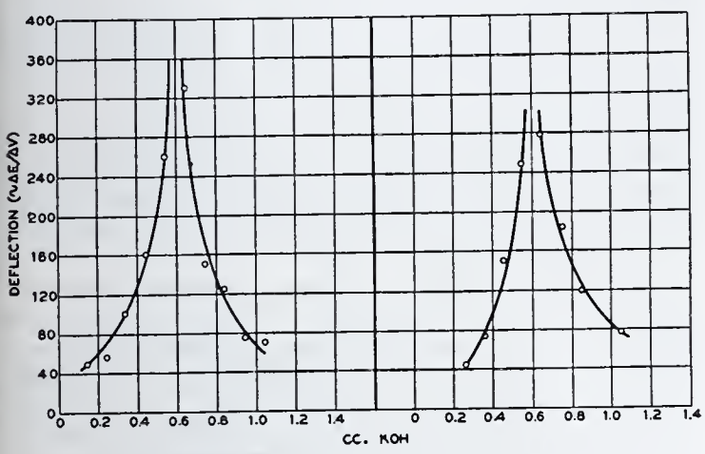


Figure 4—Titrations of Two Lubricating Oils

With R_2 adjusted until the meter needle rests at zero on the most sensitive scale, set the meter on the next higher scale. Add exactly 0.5 cc. of the reagent. Record the equilibrium deflection of the meter needle as microamperes and then set the needle back to zero. Read the buret and add a second 0.5-cc. portion of the reagent, recording the deflection as before. Proceed in this manner until a maximum deflection has been passed. This will constitute a rough titration to locate the region in which the maximum occurs. Repeat the titration using a fresh sample of proportionate weight, but running the reagent into the solution until within about 0.5 cc. of the buret reading at which the maximum should occur, as indicated in the rough titration. When this point is reached add the reagent dropwise in equal increments of approximately 0.1 cc., carrying the titration well beyond the maximum. The volume of reagent plotted against the deflection of the meter in microamperes will give curves similar to that shown in Figure 3. The peak marks the equivalence point. After a little experience has been gained with the apparatus, the end point may be estimated without plotting the curve or recording the deflections. For the highest precision it is recommended that the data be plotted. Within certain limits the precision is determined by the size of the increment (*3*).

A titration should be performed each day to determine the acidity of the solvent. This consists in following exactly the above procedure, except that the oil is not added. All titrations are corrected by subtracting the value of the blank.

Experimental Data

In Table I are given titration data obtained by titrating two 100-mg. portions of benzoic acid dissolved in 110 cc. of butyl alcohol. Plots of these data are shown in Figure 3.

Table II shows that the reproducibility of the method on standard benzoic acid is of the same order of magnitude as the error of reading the buret.

Plots for the titration data on two used lubricating oils, given in Table III, are shown in Figure 4.

Table I—Titration of Benzoic Acid Dissolved in Butyl Alcohol

Potassium Hydroxide	Deflection (~ΔE/ΔV) Titration 1	Titration 2
Cc.		
17.05	22	20
17.10	30	35
17.15	44	43
17.20	60	67
17.25	80	76
17.30	95	88
17.35	100	94
17.40	85	75
17.45	78	70
17.50	68	58
17.55	60	52
17.60	51	51
17.65	48	43
17.70	46	37
17.75	43	40
17.80	40	36
17.85	40	34
17.90	38	33

Table II—Reproducibility of Method

Titration	Potassium Hydroxide	Deviation from Mean
	Cc.	
1	17.34	−0.02
2	17.34	−0.02
3	17.39	+0.03
4	17.37	+0.01
5	17.35	−0.01
Mean	17.36	±0.02

Table III—Titrations of Two Used Lubricating Oils

Potassium Hydroxide	Deflection (~ΔE/ΔV) Titration 1	Titration 2
Cc.		
0.15	50	...
0.25	56	46
0.35	100	74
0.45	160	152
0.55	260	250
0.65	330	280
0.75	150	184
0.85	125	120
0.95	150	93
1.05	70	78

The data in Table IV show the close concordance obtainable between our method and the A. S. T. M. colorimetric method (*2*) in cases where the latter procedure is applicable. These data are especially convincing since the colorimetric results were obtained independently of the authors at the laboratory of A. E. Flowers of the De Laval Separator Company, whose courtesy in permitting the use of them is greatly appreciated.

Table IV—Comparative Data on Used Oils by Electrometric and Colorimetric Methods

Oil Sample	History	A. S. T. M. Colorimetric	Bell Lab. Electrometric	Diff.
1	Used transformer oil	1.52	1.56	−0.04
2	Artificially sludged spindle oil	0.29	0.27	+0.02
3	Artificially sludged turbine oil	0.03	0.03	+0.00
4	Used turbine oil	0.83	0.81	+0.02
5	Used crankcase oil	0.19	0.16	+0.03
6	New turbine oil	0.21	0.18	+0.03
			Mean	±0.02

There has been occasion to adapt this method to problems where organic solvents other than butyl alcohol are required, and the details of these adaptations will be published in a future paper.

Acknowledgment

The authors are indebted to A. E. Ruehle for performing part of the laboratory work on this problem, and to D. E. Avery for similar services in the early stages of the investigation.

Literature Cited

(1) Am. Soc. Testing Materials, *Proc. Am. Soc. Testing Materials*, **25**, Part 1, 282 (1925).
(2) Am. Soc. Testing Materials, Tentative Standards, p. 378, 1930.
(3) Clarke and Wooten, *J. Phys. Chem.*, **33**, 1468 (1929).
(4) Evans and Davenport, Ind. Eng. Chem., Anal. Ed., **3**, 82 (1931).
(5) Gelbach and Compton, *Ibid.*, **2**, 397 (1930).
(6) Kremann and Schöpfer, *Seife*, **6**, No. 35–38 (1922).
(7) Seltz and McKinney, Ind. Eng. Chem., **20**, 542 (1928).
(8) Seltz and Silverman, *Ibid.*, Anal. Ed., **2**, 1 (1930).

Rapid Volumetric Method for Determination of Potassium[1,2]

Loyal Clarke and J. M. Davidson

U. S. Bureau of Mines, Nonmetallic Minerals Experiment Station, New Brunswick, N. J.

During the course of development work on the extraction of potash from polyhalite, it was found desirable to develop a rapid method for the determination of potassium in solutions containing potassium and magnesium sulfates. Such a method, depending upon the precipitation and titration of potassium acid tartrate, has been developed and found to be sufficiently accurate for many purposes. The entire procedure for a single analysis may be carried out in less than 30 minutes, and as many as six determinations may be completed in 90 minutes. The method is consequently especially suited for industrial chemical control work. A modification of the method as originally developed for the analysis of potassium in solutions of potassium and magnesium sulfates has also been applied to mixtures of sodium and potassium chlorides and to potassium nitrate.

Acid Tartrate Methods Previously Used and Observations Leading to New Procedures

Several workers (*1–3*, *5–9*) have suggested acid tartrate methods for the determination of potassium. Of these, the procedures of Meurice (*6*) and Ajon (*1*) are the most promising.

The method of Meurice depends upon the precipitation of potassium acid tartrate from a solution containing potassium salts by the addition of requisite amounts of a saturated solution of sodium acid tartrate and methanol. An overnight period of standing was necessary for complete precipitation of the potassium. After filtration and washing, Meurice dissolved the potassium acid tartrate in a measured volume of standard sodium hydroxide, and finally titrated the excess of this reagent with hydrochloric acid. From this titration and the amount of base used in neutralizing and dissolving the acid tartrate, the amount of potassium present was calculated. Meurice found his method to be moderately accurate for pure potassium sulfate, chloride, or nitrate and to be unaffected by moderate amounts of magnesium or calcium. Ajon had previously developed a somewhat similar method using ethyl alcohol instead of methanol. The authors have also adopted the use of ethyl alcohol.

The method of the authors differs from previous methods (1) in the use of a mechanical stirrer to accelerate the formation of potassium acid tartrate, (2) in effecting the precipitation of the bulk of the potassium from aqueous solution before addition of alcohol which is then added with stirring at a controlled rate, (3) in the use of tartaric acid in addition to sodium acid tartrate as the precipitant, and (4) in direct titration of the potassium acid tartrate with 0.12 *N* sodium hydroxide.

About 40 pilot experiments were conducted to determine the best conditions for carrying out the analysis of potassium sulfate in solutions also containing magnesium sulfate. From this work it was found that too rapid addition of alcohol results in the precipitation of potassium sulfate which when once formed was only slowly converted to the much less soluble but slow-forming acid tartrate. Also, the best concentrations of alcohol, potassium sulfate, sodium acid tartrate, and tartaric acid to effect complete precipitation of pure potassium acid tartrate were determined. Too large an excess of sodium acid tartrate is undesirable because this salt is of limited solubility in alcoholic solutions (super-saturated solutions of the salt are readily formed, however, and are moderately stable). A considerable excess of the acid tartrate is necessary for complete precipitation of the potassium salt, especially in the presence of magnesium sulfate. The excess necessary is considerably reduced by the addition of tartaric acid.

The above observations and other data obtained in the pilot experiments led to the adoption of a satisfactory set of conditions for the analysis of potassium and magnesium sulfate solutions. This procedure will for convenience be designated as procedure I.

An attempt was made to apply the procedure to mixtures of sodium and potassium chloride. While the method was satisfactory for analysis of solutions of the latter salt, it was useless in the presence of appreciable amounts of sodium chloride, as the results were much too high. (The analysis of a single polyhalite extract which was high in salt, however, indicates that as much as 0.2 gram of sodium chloride may not interfere with the method.) Some of the sodium acid tartrate was replaced by the magnesium salt in order to obviate the difficulty. A satisfactory procedure, II, was so developed. The results using these conditions, however, were consistently low, necessitating the use of an empirical factor in order to obtain correct results. On this account the method could not be recommended as a general method for potash, but the authors feel that the method or modifications of it should prove of considerable value for routine analytical work.

The two procedures are outlined below. Procedure I was especially developed for analysis of solutions containing K^+, Mg^{++}, and SO_4^{--}, and procedure II for solutions containing K^+, Na^+, Cl^-, and NO_3^-.

Procedure I

A sample is diluted so that a 25-cc. aliquot (or a smaller aliquot later to be diluted to 25 cc.) contains 0.20 to 0.48 gram of potassium sulfate. If this sample contains 0.15 gram of magnesium sulfate or more, 20 cc. of a saturated solution of sodium acid tartrate and 5 cc. of a 20 per cent solution of tartaric acid are then added and mechanical agitation started. Within 2 or 3 minutes a crystalline precipitate of potassium acid tartrate will appear. If less than 0.15 gram of magnesium sulfate is present, more should be added, or better, only 15 cc. of saturated sodium acid tartrate and 60 cc. of alcohol should be used in the procedure, which is otherwise unaltered. Stirring should be continued for at least 2 minutes more before addition of alcohol. Then 65 ± 2 cc. of U. S. P. 95 per cent alcohol are added from a buret or a dropping funnel at a rate such that 6 to 8 minutes are required for this addition. The solution should be stirred continuously during the addition of the alcohol, and stirring should be continued 2 to 3 minutes after the addition is complete. The mixture is then immediately filtered and the crystalline potassium acid tartrate washed with not more than six small portions of wash solution prepared by mixing two parts of 95 per cent U. S. P. alcohol with one part of distilled water (four washings are sufficient to remove all SO_4^{--} from the solid).

[1] Received September 6, 1930.

[2] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Two of these washings are usually sufficient for transfer of the solid to the paper, as this transfer does not need to be quantitative. The time required for this filtration may be very materially reduced by using 9-cm. rapid filter paper fitted to a long narrow stem funnel by wetting with distilled water. The filter paper is freed from water by washing with two portions of alcohol wash solution before the filtration is begun.

After filtration and washing, the potassium acid tartrate is dissolved in nearly boiling distilled water and titrated with 0.12 *N* sodium hydroxide.

Procedure II

A sample is taken so that a 25-cc. aliquot (or a smaller aliquot later diluted to 25 cc.) contains 0.08 to 0.22 gram of potassium. If more than 0.40 gram of sodium chloride or nitrate is present, the method is not recommended. Twenty-five cubic centimeters of a solution containing 104 grams of $MgC_4H_4O_64H_2O$, 95 grams of $NaHC_4H_4O_6H_2O$, and 264 grams of tartaric acid per liter are then added to the sample and mechanical agitation started. Subsequent steps are exactly the same as those outlined for procedure I.

Comparison of New Method with Hicks Method

Procedure I has been used extensively for over a year by this laboratory for analysis of water extracts of the mineral polyhalite. These extracts contain nearly equivalent amounts of potassium and magnesium sulfates and small amounts of sodium chloride and calcium sulfate. A comparison of results obtained by this method with analysis by a modification of the chloroplatinate method of Hicks (*4*) is given in Table I.

Table I—Comparison of New Method and Hicks Method

Substance Analyzed	Magnesium Sulfate in Sample	Potassium Sulfate Found: Hicks method	Potassium Sulfate Found: New method	Difference
	Gram	*Gram*	*Gram*	%
Polyhalite extract	0.20	0.3156	0.3136	−0.7
Polyhalite extract	0.24	0.3358	0.3330	−0.8
Polyhalite extract	0.24	0.3494	0.3510	+0.5
Polyhalite extract	0.27	0.3912	0.3872	−1.0
Polyhalite extract	0.24	0.3392	0.3372	−0.6
Polyhalite extract	0.28	0.4118	0.4084	−0.8
Polyhalite extract	0.32	0.4648	0.4644	−0.1
Kali magnesia	0.17	0.2368	0.2380	+0.5
Potassium sulfate	0.01	0.2257	0.2260	+0.1
			Mean	−0.3

A comparison of the results of analysis of synthetic potassium chloride and potassium nitrate solutions by procedure II with analyses by the method of Hicks (*4*) is given in Table II. In the case of the potassium chloride solution used, the chloride content was also determined by Mohr's method, and the titer calculated as potassium checked the chloroplatinate procedure to 0.1 per cent.

Table II—Comparison of Procedure II with Hicks Method

Form of Potassium in Sample	Sodium Chloride in Sample	Potassium Found: Hicks method	Potassium Found, Procedure II: Calcd. by theoretical factor	Potassium Found, Procedure II: Calcd. by empirical factor[a]	Difference
	Gram	*Gram*	*Gram*	*Gram*	%
KCl	None	0.1038	0.1015	0.1032	−0.6
KCl	None	0.1038	0.1022	0.1038	−0.0
KCl	None	0.1038	0.1023	0.1040	+0.2
KCl	None	0.2076	0.2040	0.2074	−0.1
KCl	None	0.2076	0.2027	0.2060	−0.8
KCl	0.40	0.1038	0.1023	0.1040	+0.2
KCl	0.40	0.1038	0.1016	0.1032	−0.6
KCl	0.40	0.2076	0.2040	0.2074	−0.1
KCl	0.40	0.2076	0.2050	0.2083	+0.3
KNO_3	None	0.1960	0.1933	0.1964	+0.2
KNO_3	None	0.1960	0.1933	0.1964	+0.2
KNO_3	None	0.0983	0.0974	0.0990	+0.4
KNO_3	None	0.0983	0.0972	0.0988	+0.3
KNO_3	None	0.0983	0.0970	0.0986	+0.2
KNO_3	None	0.0983	0.0968	0.0984	+0.1

[a] Empirical factor used is 1.016 times theoretical factor.

Reference to this table shows that if the empirical factor of 1.016 times the theoretical is used, the results of the procedure agree fairly satisfactorily with the results of the chloroplatinate procedure.

Acknowledgment

The authors wish to acknowledge the valuable suggestions of Nathan Fragen, junior chemist, of this laboratory.

Literature Cited

(1) Ajon, *Ann. staz. sper. di agrumicoltura e frutticoltura di Acireale*, **3**, 91 (1915).
(2) Bayer, *Chem.-Ztg.*, **17**, 686 (1893).
(3) Bokemuller, *Chem. Zentralblatt*, **1918**, II, 764.
(4) Hicks, J. Ind. Eng. Chem., **5**, 650 (1913).
(5) Marshall, *Chem.-Ztg.*, **38**, 585 (1914).
(6) Meurice, *Ann. chim. anal. appl.*, **7**, 161 (1925); **8**, 130 (1926).
(7) Okada, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 89 (1914).
(8) St. Minovici and Kolla, *Bul. soc. chim. România*, **3**, 25 (1921).
(9) Touaritske and Slezak, *Zhurnal Sakharnoi Prom.*, **2**, 462 (1928).

Method for Increasing Sensitivity of Certain Chemical Test Reactions[1]

Irwin Stone

360 Wadsworth Ave., New York, N. Y.

THE general class of organic precipitant reagents used in qualitative inorganic analysis includes some of the most sensitive chemical tests for metals known. Some, such as the dimethylglyoxime test for nickel, are well known, whereas others, such as the *p*-nitrobenzeneazoresorcinol test for magnesium (*4*), or the *p*-dimethylaminobenzylidenerhodanine test for silver (*2*) have not such widespread recognition.

The usual reaction that takes place in this class of tests is one where the metal enters the molecule of the organic compound to form a very insoluble, highly colored precipitate. This precipitate, composed of a generally water-insoluble organic residue coupled to a metal, which is more or less repelled by organic solvents, forms a typical polar molecule. This polar precipitate, if shaken with a mixture of water and some immiscible organic solvent, will tend to collect at the water-solvent interface, the molecules probably orienting themselves similar to the polar molecules described by Harkins and his co-workers (*1*) and Langmuir (*3*), the organic portion jutting into the immiscible solvent phase while the metallic portion points toward the water.

This fact may be applied to extending the range of sensitivity of these tests by collecting at the interface the small amount of precipitate which would be undiscernible suspended in the large bulk of test liquor. It may also be utilized to make faint reactions more easily and surely recognizable.

As a general method for performing this sensitization, one may conduct the test in the usual manner and when completed add a few cubic centimeters of ether and shake thoroughly. When the ether has separated, note any color or precipitate that has collected at the water-ether interface.

[1] Received April 27, 1931.

Table I—Sensitivity of Organic Precipitant Reagents

Metal	Reagent	Sensitivity Usual method	Sensitivity Interface method
		Mg. per 5 cc.	
Nickel	Dimethylglyoxime	0.02	0.005
Aluminum	Alizarin	0.5	0.01
Magnesium	*p*-Nitrobenzeneazoresorcinol	0.07	0.01
Silver	*p*-Dimethylaminobenzylidenerhodanine	0.001	0.00008

Table I shows the increase in sensitivity for a few organic precipitant reagents. The figures in the table are not to be construed as accurate sensitivity figures, but merely the limits of an easily discernible reaction under similar conditions.

Literature Cited

(1) Harkins et al., *J. Am. Chem. Soc.*, **39**, 354 (1917); **39**, 541 (1917); **42**, 700 (1920); **43**, 35 (1921).
(2) Kolthoff, *Ibid.*, **52**, 2222 (1930).
(3) Langmuir, *Ibid.*, **39**, 1848 (1917).
(4) Ruigh, *Ibid.*, **51**, 1456 (1929).

Studies on Turbidity in Sugar Products

I—Relation between Intensity of Tyndall Beam and Depth and Concentration of Solution[1]

F. W. Zerban and Louis Sattler

New York Sugar Trade Laboratory, Inc., 80 South St., New York, N. Y.

Previous work on the optical measurement of turbidity in general, and with respect to sugar products in particular, is briefly reviewed. The Pulfrich photometer, with which both the transmittancy and the Tyndall-beam intensity of turbid solutions can be determined, is described. Several series of such measurements have been made on a raw sugar solution at varying depths and concentrations. It was found that with colored turbid solutions the Tyndall-beam intensity is affected to such an extent by absorption that the latter must be corrected for. The ratio between Tyndall-beam intensity and transmittancy is within a certain range, a power function of the depth or the concentration, according to the formulas $R = R_1 \times b^n$, and $R = R_1 \times c^n$, where b is the depth, c the concentration, R_1 the ratio for unit depth or concentration, and R the ratio at any depth or concentration; n is a constant which, at constant depth and varying concentration, or vice versa, is independent of wave length. In the formula $R = R_1 \times b^n$, the value of n varies approximately as the logarithm of the concentration. The work is being continued to test the above formulas further and combine them into one equation.

Turbidity plays an important part in the manufacture of cane sugar. The juice expressed from the cane contains suspended matter in various degrees of dispersion, from coarse, through fine particles, to those of colloidal dimensions. One of the objects of clarification is to remove the suspended matter as far as possible. Even if this object has been attained, the juice becomes cloudy once more upon concentration, and the sirup must again be settled before crystallization, because any suspended matter is partly adsorbed on the crystals, partly retained on them while the sugar is being centrifuged, and another important part goes into the runoffs. When these are boiled to grain, the cycle is repeated, and when a low-grade sugar in which suspended matter has accumulated is used as seed, the resulting sugar gives a very turbid solution. In raw sugar manufacture, the juices, sirups, and molasses are not filtered, but only settled, and the care with which this is done largely determines the filtering quality of the raw sugar. Turbidity in the liquors of the refinery causes similar difficulties as in the raw sugar factory, and the suspended particles must be removed in order that a product of high quality may be obtained which must be free not only from color and dissolved impurities, but must also give a clear solution. If turbidity is to be controlled in the factory, we must be able to measure it.

Turbidity measurements would also prove of value in various analytical operations. The suspended matter in juices, sirups, and molasses affects the specific gravity of the latter. To correct for this, it is customary to let the solution stand until the suspended matter has settled out. The nonsettling particles should also be allowed for because they influence the specific gravity. Their quantity can probably be determined more easily by a simple turbidity determination than by filtration and weighing, as is the custom at present. As a further example, the problem of color determinations in sugar products may be mentioned. Various investigators have found that in order that the Lambert-Beer law may be applied to such measurements, the turbidity must be reduced to a certain minimum by careful filtration. It is not known exactly what that minimum should be, except that there should be only a faint Tyndall beam. Opinions differ as to what is the best filtering medium to use. A careful study of turbidity and transmittancy of solutions may be expected to throw more light on this disputed point.

These few examples will suffice to show the importance of turbidity measurements in the sugar industry.

Available Radiometric Procedures

The radiometric procedures available for this purpose fall into three classes.

In the first of these, the measurements are made by transmitted light, using a photometric null device and comparing either with a standard dispersion in the same dispersion medium (turbidimeters of the Duboscq colorimeter type), or comparing with the intensity of the light transmitted by the dispersion medium or a standard dispersion in a second absorption cell of the same characteristics (photometers, spectrophotometers). This group of methods is especially adapted for measuring visible turbidity.

The second group is based on measurements with a photometric null device of the intensity of the Tyndall beam emitted by the dispersed particles, in a manner similar to the one used in transmittancy measurements. If the comparison is made with a standard dispersion, the instruments are termed nephelometers; if the comparison is made directly with the intensity of the incident light they are called tyndall-

[1] Received April 14, 1931. Presented before the Division of Sugar Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

meters (*8*). These two types of instruments are used particularly for determining invisible turbidities, but their range extends also into visible turbidities. The first two groups, which depend on the photometric principle, are free from personal errors so long as substantially monochromatic light is used, or the spectral curves of the two solutions to be compared are substantially the same.

The third group of methods employs the criterion of complete extinction, and is thus subjective in character. The depth at which an object, such as a wire or a small light, placed in or behind the column of liquid becomes invisible, serves as a measure of the turbidity. This method of procedure is to some extent independent of the color of the solution, but is subject to considerable error due to differences in the acuity of vision of different observers.

Nearly all of the experimental work on the transmittancy of turbid liquids has been done on dispersions in colorless media, or by comparison with standards prepared with the same dispersion medium, so that the light absorption due to the latter was compensated for. Even under these conditions, the Lambert-Beer law, usually valid for molecularly dispersed systems, does not generally hold. The negative logarithm of the transmittancy does not increase at the same rate as the depth and concentration, but is a power function of these two variables. The Lambert-Beer formula, with the exponent equal to 1, is but a special case of the more general equation. If a certain instrument nevertheless shows a linear relationship between optical density and depth or concentration, this is generally due to the characteristics of its construction.

The rate of change of the Tyndall intensity with depth and concentration, utilized in nephelometers and tyndallmeters, is much more complicated than that of the optical density of the turbid solutions. Wells (*8*) has developed a complete formula for the Tyndall intensity ratio, assuming perfectly diffused light. This formula contains eight constants and is not serviceable for practical purposes. For this reason it is often preferred to calibrate such instruments empirically for each type of solution to be investigated. For very low concentrations and depths, the calibration curve may be a straight line within the limits of error. This is shown, for instance, in the data of Tolman and co-workers (*7*) for a silica suspension up to a concentration of one gram per liter. The curve then bends asymptotically, and Wells (*8*) has shown that the exponential formula given above for transmittancy measurements fits the experimental results of several investigators quite closely. In Tolman's silica suspension, the curve reached a maximum at around 2.5 grams per liter, and then the Tyndall intensity decreased with rising concentration because the light absorption overbalanced the Tyndall effect.

The extinction method of measuring turbidity is based on the assumption that the simple dilution law holds. In reality, the conditions are much more complex, as has also been shown by Wells. In practice, each instrument must be calibrated empirically for each type of dispersion to be measured.

A choice between different instruments must be based primarily on the character of the turbid systems. For dispersions of very low concentrations, particularly those which appear clear by transmitted light, tyndallmeters or nephelometers must be used, as this is by far the most sensitive method. Even carefully purified water shows a distinct Tyndall cone when the light source has sufficient intensity. For medium concentrations, readings by transmitted light may be substituted. The extinction criterion permits of the greatest range in visible turbidity, but as has been stated above, it has other limitations because it is a subjective method greatly influenced by personal error.

So far, only dispersions in which the light absorption due to the dispersion medium is negligible, or corrected for by direct comparison with a standard dispersion in the same medium, have been considered. This condition can rarely be met in the sugar industry. In technical sugar products, turbidity and coloring matter vary independently, and for this reason it is impossible to select any one standard turbid solution applicable to all products.

Nevertheless, the need for turbidity measurements on sugar products has been so obvious that many attempts have been made to solve this problem. Several of the types of methods described above have been resorted to.

Description of Various Existing Turbidimeters

A common procedure, largely employed in Hawaii and in the Philippines, for determining the clarity of juices and of raw sugar solutions, is based on the extinction criterion. The Kopke turbidimeter is an illustration of this principle. It is assumed that the simple dilution law holds, but it is evident from the discussion presented above that this apparatus can at best give only approximately relative values which are not a linear function of the turbidity. Furthermore, it is very difficult for different observers, working independently, to check each other's readings.

The Jackson turbidimeter, recommended by Lindfors (*5*) for measurements of invisible turbidity, is also based on the extinction criterion. This instrument permits greater precision in the readings than the Kopke turbidimeter, but otherwise has the same limitations.

Colorimeters of the Duboscq type and nephelometers of similar construction do not seem to have been employed for turbidity measurements in sugar products because of the complications due to the presence of coloring matter.

The Tyndall phenomenon has been made use of in another way by several investigators. The turbidiscope of Horne and Rice (*3*) is based on this principle. It is admittedly meant only for rough comparisons, as no attempt was made in the original design to compensate for differences in the concentration of coloring matter. Lindfors (*5*) has recommended this apparatus and has improved the method of using it to obtain more nearly quantitative results. A series of turbidity standards is made up by dispersing bentonite in water, and sufficient caramel solution is added to each so that the color of the solution in all the tubes approaches that of the unknown. Lindfors further proposed to replace the slit of uniform width in the original instrument by slits of varying width, so that the results obtained by dilution may be checked by those based on varying depth.

An ingenious apparatus for measuring turbidities of low concentration has been described by Ingersoll and Davis (*4*). The effect of color is overcome to a large extent by exciting a Tyndall beam of only 1 mm. thickness horizontally at zero depth—that is, at the surface of the liquid in an absorption cell open at the top. A measuring tube with concentrated potassium dichromate solution is placed above the Tyndall beam and the depth of dichromate solution determined at which the cone becomes invisible. In other words, the extinction criterion is used to measure the Tyndall intensity. A red filter is placed in the primary beam to exclude fluorescence effects, and a Wratten filter No. 29F is interposed between the surface of the liquid of the absorption cell and the dichromate solution. When turbid liquors are diluted with practically cone-free water or white sugar sirup, the depth of the dichromate solution is a linear function of the turbidity, except at the lowest concentrations where the curve ascends more steeply. This straight-line relationship is of advantage in practice. No experimental proof has been furnished that with this apparatus the turbidity in solutions of varying color is directly proportional to the readings.

A simple and practical differential method of turbidity

determination in sugar products has recently been developed by Balch (*1*). The turbid sugar solution is compared directly with a filtered portion of the same solution in a spectrophotometer, and the specific absorptive index is taken as a measure of the turbidity. Unlike the method of Ingersoll and Davis, this procedure is applicable only to turbidities of sufficient magnitude to affect the transmittancy appreciably. It is interesting to note that equal concentrations of suspended matter in a water-white solution and in a dark-colored caramel solution gave the same reading; this shows that the color of the solution is effectively compensated for. Balch proved experimentally that the Lambert-Beer law does not hold strictly for the suspended matter, but he states that the results give a good approximation. Honig (*2*), who used essentially the same method, also calls attention to the fact that the results obtained are only relative.

The data given by Balch in Table I of his paper show that for this particular suspension Beer's law holds quite closely. But there is a gradual increase in the values of $(-\log T)/c$ from 0.074 for the lowest concentration, taken as the unit, to 0.080 for the highest concentration. If the T values actually read are substituted in the more general formula $-\log T = (-\log T_1) \times c^n$, the numerical value of n is found to be 1.032—that is, a trifle higher than the exponent 1 for Beer's law.

It must be considered, however, that the transmittancy of turbid media is influenced by the characteristics of the primary beam and also by the shape and width of the absorption cell used. For this reason the readings obtained on a certain instrument with one type of cell do not necessarily agree with readings for the same solution in another instrument with a different type of cell.

Description of Improved Instrument

As the problems of the sugar industry call for measurements of color as well as of visible and invisible turbidity, it would be desirable to have an instrument, preferably moderate in price, with which all these measurements could be made interchangeably. The usual spectrophotometers are suitable for two of these types of measurement—that is, of color and of visible turbidity. The tyndallmeter of Mecklenburg and Valentiner is not equipped for transmission measurements and is very expensive. Recently a photometer originated by Pulfrich (*6*) has been placed on the market by Carl Zeiss; this may be used as a colorimeter or turbidimeter like the Duboscq type of apparatus, or as a photometer for measurements with transmitted or reflected light, and of Tyndall intensity. Auxiliary equipment is furnished for determining gloss and fluorescence, and for specifying colors by the monochromatic or trichromatic system. The instrument has no dispersing prism, but color filters with fairly narrow spectral bands are used. This disadvantage is, however, largely offset by the features already mentioned, and also by the fact that the same glass cells are employed for both transmittancy measurements and determinations of Tyndall intensity. This is important because the edge effects caused by the shape and width of the cells are thus the same in the two types of measurements. The reference standard for Tyndall intensity is a turbid glass block which is calibrated by the manufacturers on the basis of the intensity of the light source under the same conditions under which the instrument is used. The values obtained can thus be expressed in absolute intensity ratios if desired, but this will be necessary only for intercomparisons of measurements made with different standard blocks.

The construction of the photometer and some of its accessories will be only briefly outlined because complete descriptions have been published by the manufacturers. The photometer can be placed either vertically to be used as a colorimeter and for reflectance measurements, or horizontally for determining transmittancies or Tyndall intensities. At the objective end it has two openings with centers 7 cm. apart. Each of the two apertures is formed by two V-shaped shutters moving symmetrically in opposite directions, with their planes in direct contact. The area of the aperture is varied, and at the same time measured by means of drums mounted on the sides. The peripheries of the drums are calibrated in per cent transmission. The peculiar V-shaped construction of the shutters causes the percentage divisions to be much farther apart near the zero point than near the one hundred point. This makes it possible to read small transmissions with greater precision than when the percentage units are equidistant. Since both apertures may be varied independently, either one may be set at one hundred, and the samples may be reversed. The beams passing through the two apertures are brought into juxtaposition in the field of vision by a system of prisms and lenses. The color screens are placed in a revolving drum mounted in the ocular, and may be turned into the field in regular order. Eight color filters, covering the spectrum from the extreme blue to the extreme red end, are furnished for transmission measurements, and three less dense filters are supplied for the Tyndall-intensity determinations.

For transmission measurements up to a depth of 30 mm., the absorption cells are placed in holders fastened to the rear of the photometer apertures. If longer absorption tubes are required, they are placed on a special stand between the photometer and the light source. The lamp house is hemispherical. It has two circular openings in front, with centers 7 cm. apart to correspond with the photometer apertures. It furnishes two parallel beams of equal intensity. The light may be diffused by frosted glass disks.

If the instrument is to be used for the measurement of Tyndall intensity, the lamp house and cell holders are removed and an auxiliary apparatus placed against the rear of the photometer in its horizontal position. This attachment consists essentially of a cylindrical housing, and is constructed in such a way that no stray light can enter the photometer. On the side opposite the left photometer opening is a cylindrical chamber. Behind this and somewhat to the right is the lamp, placed so that the primary beam of light passes through a square opening in the wall of the compartment and then through the sample at an angle of 45 degrees from the direction of the observation. The angle of 45 degrees was chosen because this furnishes greater Tyndall intensity than the usual angle of 90 degrees. The cell is placed in a holder in such a position that the primary beam strikes the rear face normally, whereas the front face is sighted obliquely through the left photometer aperture. The actual measurements are made by substitution in order to eliminate errors due to inequalities in the intensity of the light beam passing through the sample and that of the comparison beam. The latter goes through any one of four milk glasses of different optical densities. The sample is measured against the glass which furnishes the smallest difference in intensity from that of the sample. Then the sample is removed, the standard block is substituted for it, and this is now measured against the same milk glass used in case of the sample.

The ratio between the intensity found for the sample and that for the standard furnishes a relative measure of the Tyndall intensity of the sample. The readings are taken with a color filter, blue, green, or red, interposed in the ocular. Their effective wave lengths were found to be 449, 529, and 621 mμ, respectively. These wave lengths were obtained by determining with the Keuffel and Esser color analyzer, the spectral-transmittancy curve of a carefully filtered raw sugar solution. The transmittancy of the same sugar solution was also measured with the Pulfrich photometer for the three

color filters, and the effective wave lengths of the screens found by locating the transmittancies observed on the spectral-transmittancy curve of the solution.

Comparison between Tyndall Intensity and Transmittancy with Pulfrich Photometer

The primary object of the present investigation is to ascertain the properties of turbid and colored sugar solutions with respect to both transmitted and scattered light, with the use of the spectrophotometer as well as of the Pulfrich photometer. The first problem selected is a comparative study of the Tyndall intensity and transmittancy of such solutions with the Pulfrich photometer. Balch's spectrophotometric method for measuring turbidity by transmitted light has already been mentioned. The Pulfrich instrument, equipped with a monochromatic light source, can be used for this purpose, but it remains to be seen with what precision this can be done when light filters are used instead of spectrally purified light.

Experimental data on the relation between Tyndall intensity of highly colored turbid media and the depth and concentration of such dispersions have not been found in the literature and must be supplied before the problem of turbidity determinations, based on Tyndall intensity in media of varying color, can be attacked. The technic involved demands the greatest scrupulousness and care. Absolute cleanliness is essential, even more so than in transmittancy measurements, since the Tyndall phenomenon is a much more sensitive criterion.

Much preliminary work had to be done. The cell holder furnished by the manufacturers was equipped only for the 2.5-mm. cell, and a special holder had to be constructed which accommodates cells of smaller and greater depths up to about 25 mm.

A dark-colored raw sugar was used to establish the relation between Tyndall-beam intensity and depth of solution. The large number of factors which can disturb both the color and turbidity values of a given sample make it imperative that a uniform system be adopted for the preparation of the sample for examination.

The sugar is weighed out in a wide-mouth Erlenmeyer flask, and enough boiling hot distilled water is added on the balance to bring the solutions slightly above 60° Brix. The Erlenmeyer flask is placed in a beaker of water at 80° C., and the contents stirred gently. It was found that a total heating time of 15 minutes was adequate for the size of samples employed in this laboratory. These averaged around 40 grams of sugar. After the sugar is in solution it is cooled quickly to room temperature, and coarse, suspended particles, such as bag fibers, scale, etc., are removed by whirling for 15 minutes in a small hand centrifuge at 1100 r. p. m. Finally, the density is adjusted to 60° Brix by refractometer.

Other solutions were made by mixing the original solution in various proportions with a white sugar sirup of 60° Brix, decolorized with Suchar, and carefully filtered with barium sulfate of x-ray grade and with specially purified asbestos. As it is well known that such solutions containing complex colloidal systems and subject to attack by enzymes do not keep for any length of time, it was necessary in each series of measurements at varying depth to prepare a fresh solution from a different portion of the same raw sugar. The readings for each series are therefore strictly comparable only as to varying depth, but not so far as varying concentration is concerned. The Tyndall-intensity readings on solutions containing 6, 15, 24, 54, and 77.1 grams of colored dry substance are shown in Table I.

With solution 1, red screen, the Tyndall intensity increases steadily with depth. In most of the other series it first increases, reaches a maximum, and then drops again. In solutions 4 and 5, blue screen, the maximum has already been reached at a depth less than 1.06 mm., and the figures descend from the very beginning. Although theoretically the Tyndall intensity itself would steadily increase with depth if there were no absorption, this increase is counteracted by the growth in absorption as the depth becomes greater. To ascertain the magnitude of this effect, it was necessary to determine also the transmittancies of the same solutions in the same cells. This gave the results assembled in Table II.

Table I—Tyndall Intensity Readings at Varying Depth

Depth	1	2	3	4	5
			BLUE SCREEN		
Mm.					
1.06	35.2	60.4	132.2	161.2	184.2
2.53	68.1	124.0	201.7	148.6	130.8
5.09	93.4	152.8	158.5	72.6	31.8
10.01	115.3	113.3	81.1	9.32	1.43
20.06	76.4	34.6	12.1	..	..
			GREEN SCREEN		
1.06	129.6	168.5	429.1	794.4	931.0
2.53	201.7	421.9	926.8	1210	1042
5.09	288.6	615.4	1306	1131	818.0
10.01	502.3	943.8	1100	357.6	141.9
20.06	445.7	324.2	292.3	128.6	3.69
			RED SCREEN		
1.06	393.8	640.1	1435	2014	3342
2.53	665.2	1430	3259	4884	3753
5.09	1050	2659	5455	6783	6426
10.01	1824	3816	6323	5363	4373
20.06	1861	3286	3779	1133	737.4

Table II—Transmittancies of Same Solutions at Varying Depths

Depth	1	2	3	4	5
			BLUE SCREEN		
Mm.					
1.06	90.8	81.8	74.5	48.5	35.0
2.53	79.2	60.5	46.3	17.6	8.44
5.09	66.2	37.4	16.0	3.2	0.78
10.01	47.7	15.9	4.8	0.13	...
20.06	20.9	2.63	0.36	...	...
			GREEN SCREEN		
1.06	95.3	89.8	82.3	67.1	57.0
2.53	89.0	75.4	64.5	37.1	23.9
5.09	79.0	55.9	35.5	14.1	5.80
10.01	64.3	34.6	19.1	2.20	0.42
20.06	41.6	12.1	3.61	...	...
			RED SCREEN		
1.06	96.5	94.1	89.9	79.8	71.4
2.53	92.1	84.7	76.7	55.5	43.8
5.09	88.2	71.7	54.4	32.5	20.0
10.01	76.8	52.4	38.9	11.7	4.54
20.06	56.0	28.8	14.2	1.42	0.24

To save space, the corresponding values of $(-\log T)/b$ are not given here. They have been calculated, however, and the results show that the precision of the instrument is not so high as might be desired, especially in the readings near the hundred point. This is no doubt largely owing to the fact that spectral bands are used instead of spectrally purified light. The relation between $-\log T$ and depth is nearly linear, proving a close approximation to Beer's law. If the calculations are made on the basis of the formula $-\log T = (-\log T_1) \times b^n$, the average value of n is found to be 0.981—that is, slightly less than unity.

The next step was to ascertain in what way the Tyndall intensity must be corrected for absorption, and it was found that when the former is divided by the corresponding transmittancy, the resulting figures, instead of rising and falling as the Tyndall intensities do, increase steadily with the depth. A further examination showed that the ratio between Tyndall intensity and transmittancy is a power function of the depth. When the logs of the ratios were plotted against the logs of the depths, straight lines were obtained within a certain range.

From the straight-line relationship between the logs of the ratio as defined above and the log of the depth, it was concluded that the general formula, $R = R_1 \times b^n$, is applicable, where R is the ratio for any depth, and R_1 that for unit depth. The millimeter was chosen as the unit. It was found that with each separate solution the value of n was the same for all

three wave lengths, within the experimental error. This would indicate that the differences in the transmittancies at different wave lengths observed by Balch, are compensated for by similar differences in the Tyndall ratios at different wave lengths.

With the experimental data as a basis, the numerical value of n was found to be 0.726 for solution 1; 1.080 for solution 2; 1.179 for solution 3; 1.268 for solution 4; and 1.312 for solution 5. Although it has been emphasized that the five solutions of differing concentration cannot be compared directly, it is nevertheless interesting to note that the values of n vary approximately as the logs of the concentration of the colored dry substance. The calculated values for R_1 are given in Table III. These figures and those for n were substituted in the formula shown above, and the results for R at different depths, calculated in this manner, are also shown in the same table, together with the ratios actually observed.

Table III—Percentage Ratio between Tyndall Intensity and Transmittancy for Varying Depth

(Found, and calculated by formula $R = R_1 \times bn$)

Depth		1	2	3	4	5[b]
		BLUE SCREEN				
Mm.						
[a]	Calcd.	0.435	0.686	1.52	2.83	4.89
1.06	Found	0.388	0.738	1.77	3.33	5.50
	Calcd.	0.454	0.730	1.63	3.05	5.28
2.53	Found	0.860	2.05	4.36	8.45	15.2
	Calcd.	0.853	1.87	4.55	9.19	16.5
5.09	Found	1.41	4.09	9.91	22.7	42.9
	Calcd.	1.42	3.98	10.4	22.3	41.3
10.01	Found	2.42	7.13	16.9	74.0	
	Calcd.	2.32	8.25	23.0	52.6	
20.06	Found	3.66	13.2	34.0		
	Calcd.	3.84	20.8	52.3		
		GREEN SCREEN				
[a]	Calcd.	1.25	2.00	5.03	10.4	18.2
1.06	Found	1.36	1.88	5.21	11.8	19.3
	Calcd.	1.31	2.13	5.39	11.2	19.6
2.53	Found	2.27	5.60	14.4	32.6	58.3
	Calcd.	2.46	5.45	15.0	33.8	61.5
5.09	Found	3.65	11.0	36.8	80.2	164
	Calcd.	4.08	11.6	34.3	82.0	154
10.01	Found	7.81	27.3	57.6	163	402
	Calcd.	6.67	24.1	76.1	193	373
20.06	Found	10.7	26.8	81.0		
	Calcd.	11.1	60.6	173		
		RED SCREEN				
[a]	Calcd.	3.91	6.26	14.6	25.4	45.3
1.06	Found	4.07	6.80	16.0	25.2	51.5
	Calcd.	4.08	6.66	15.7	27.4	48.9
2.53	Found	7.22	16.9	42.5	88.0	155
	Calcd.	7.67	17.1	43.7	82.5	153
5.09	Found	11.9	37.1	100	209	359
	Calcd.	12.8	36.3	99.6	200	383
10.01	Found	23.8	72.8	163	458	1086
	Calcd.	20.8	75.3	221	472	930
20.06	Found	33.2	114	266	798	4058
	Calcd.	34.5	190	502	1140	2316

[a] R_1 (R for 1 mm.).
[b] Averages of two series of measurements.

In the case of the most dilute solution, number 1, there is good agreement between found and calculated values for all thicknesses. As the concentration increases, the deviations become greater, first for the 20-mm. cell, and then also for the 10-mm. cell. Up to a thickness of 5 mm. there are good checks at all concentrations. The deviations are readily explained. In the first place, the simple power formula is only a first approximation, covering a limited range. Secondly, photometric readings near the one hundred point are uncertain, and near the zero point the possible percentage error is large. Thirdly, errors in both the Tyndall intensity and in the transmittancy measurements are reflected in the ratio between the two, and they may give a combined error in the same direction. Fourthly, it has been observed that when the thick cells, of 10- and 20-mm. depth, are used for Tyndall readings, there are reflection effects from the side walls of the cells which, as has been explained above, are set at an angle of 45 degrees. It follows that with this particular instrument measurements of Tyndall intensity should be confined to cells not over 5 mm. thick.

The power law which has been found to govern the relation between the ratio R and the thickness also holds with respect to concentration and under the same limitations. Four different concentrations were used—namely, a 60° Brix solution of raw sugar, and portions of this same solution diluted in three proportions with a 60° Brix white sugar sirup which had been purified as stated previously. The colored dry-substance concentrations were 9, 18, 36, and 77.1 grams in 100 ml., respectively. The thickness of the cell was 5.09 mm. Table IV shows the found and calculated values for R, on the basis of $n = 1.470$, R_1 (concentration = 1 gram of colored dry substance in 100 ml.) for the blue screen = 0.0582, for the green screen = 0.1950, and for the red screen = 0.4626. A correction was applied for the slight Tyndall turbidity of the white sirup.

Table IV—Percentage Ratio between Tyndall Intensity and Transmittancy for Varying Concentrations

(Found, and calculated by formula $R = R_1 \times c^n$)

Concn. in 100 ml.	Found	Calculated
Grams		
	BLUE SCREEN	
9	2.01	1.77
18	4.75	4.41
36	10.6	11.6
77.1	42.7	34.6
	GREEN SCREEN	
9	5.77	5.93
18	15.8	14.8
36	38.6	38.9
77.1	154	116
	RED SCREEN	
9	15.2	14.1
18	35.3	35.1
36	90.6	92.3
77.1	354	275

Good agreement is shown between found and calculated values for the first three concentrations, but the calculated figures for the highest concentration are much lower than those observed. Some other series which were run with cells of smaller and of greater depth gave erratic results which were so evident that no calculations have been attempted. It was found subsequently that it is difficult to obtain a perfectly homogeneous mixture of the two sirups.

If the sample has been shaken violently, as for example, where the solution has been diluted with white sugar sirup, it is necessary to allow the colloids to reach equilibrium. The following figures show the magnitude of change immediately on shaking a sample violently:

	Turbidity Before shaking	Turbidity After shaking	Per Cent of Original
	%	%	
Blue	18.7	28.0	149.8
Green	506.3	744.5	147.2
Red	610.5	992.1	162.6

In the continuation of this work, colored turbid solutions of smaller specific gravity will be used, as has been done by Lindfors and by Balch. This will make it easier to vary color and turbidity independently.

Literature Cited

(1) Balch, Ind. Eng. Chem., Anal. Ed., **3**, 124 (1931).
(2) Honig, *Arch. Suikerind.*, **37**, III, 231 (1929).
(3) Horne and Rice, Ind. Eng. Chem., **16**, 626 (1924).
(4) Ingersoll and Davis, *Ibid.*, Anal. Ed., **2**, 248 (1930).
(5) Lindfors, Ind. Eng. Chem., **17**, 1155 (1925).
(6) Pulfrich, *Z. Instrumentenk.*, **45**, 34, 61, 109 (1925).
(7) Tolman, Reyerson, Vliet, Gerke, and Brooks, *J. Am. Chem. Soc.*, **41**, 300 (1919).
(8) Wells, *Chem. Rev.*, **3**, 331 (1927).

Availability of Phosphoric Acid in Ammoniated Superphosphates

Proposed Method for Estimation[1]

K. Kitsuta and Robt. M. Salter

Ohio Agricultural Experimental Station, Wooster, Ohio

Maximum solubility of phosphoric acid was obtained from the water-insoluble residues of the ammoniated superphosphates when 0.1 gram of the sample was used in 100 cc. of citrate solution for 30 minutes at 65° C. Similar results were obtained using a 2-gram sample in 100 cc. of citrate solution containing 4 grams of ammonium oxalate and digesting for 2 to 4 hours.

Attempts to shorten the time of digestion to 30 minutes by addition of larger quantities of ammonium oxalate were successful with highly ammoniated superphosphates, but the method does not apply well to ammoniated superphosphates which contain less than 2.5 per cent ammonia.

There was no noticeable decrease in the availability of the P_2O_5 of ammoniated superphosphates to buckwheat and barley when the material contained as high as 6.2 per cent ammonia.

THE rapid adoption of the superphosphate ammoniation process by the fertilizer industry makes desirable a full knowledge of the chemistry of the process and of the economic value of the product. The present report deals with the results of studies, by both chemical and plant methods, of the availability of phosphoric acid in ammoniated superphosphates of varying degrees of ammoniation.

Considerable work has been done recently by Keenen (*6*), Ross and his associates (*5*, *7*), and Howes and Jacobs (*4*), and Buie (*3*) has carried out experiments on cotton. It is known that with increase in ammoniation there occurs a decrease in the content of available P_2O_5 as measured by the present official method (*1*).

The Association of Official Agricultural Chemists tentatively approved a change in the present method (*2*) for determining water-soluble and citrate-insoluble P_2O_5 in fertilizer, whereby the sample taken for both is reduced to 1 gram and the time of digestion with citrate solution increased to 1 hour. However, this change cannot go into effect before it is officially adopted by the Association. The probability of such action being taken at next year's meeting will depend upon the results of further referee work already planned.

Experimental Procedure

Preparation of Ammoniated Superphosphates—Ammoniated superphosphates of different degrees of ammoniation were prepared in two ways. In one case the calculated amounts of dilute aqueous ammonia were introduced into a jar containing the superphosphate, after which the material was well mixed, dried, and ground. The second method employed consisted in introducing the calculated amount of ammonia gas from an ammonia generator into an evacuated flask containing the superphosphate, with thorough shaking during the ammoniation process. Samples of these ammoniated superphosphates of equal ammonia content prepared by the two methods showed by analysis nearly the same amounts of water-soluble and citrate-insoluble P_2O_5, as illustrated in Table I. Accordingly it was believed unnecessary to use both materials in the availability studies. Hence only ammoniated superphosphates prepared by the first method were employed.

Effects of Varying Weight of Sample Added to 100 cc. of Citrate Solution—Water-soluble and citrate-insoluble P_2O_5 of both superphosphates and ammoniated superphosphates of varying ammonia content were determined, using 2.0, 1.0, 0.5, 0.2, and 0.1 gram of sample per 100 cc. of citrate solution. The data are presented in Table II. It is observed that the amount of citrate-insoluble P_2O_5 decreases with a reduction in the weight of sample taken. With material containing 2.6 per cent and less of ammonia, varying the sample weight does not change the amount of available P_2O_5, owing to the fact that although there is some increase in water-soluble P_2O_5 with smaller samples, this is accompanied by a corresponding decrease in citrate-soluble P_2O_5. With ammoniation above this point there is observed a rapid increase in citrate-soluble P_2O_5 as the sample size decreases, especially in the most highly ammoniated materials, while the water-soluble P_2O_5 does not change appreciably. The proportions of available P_2O_5 to the total P_2O_5 are shown in Table III.

Table I—Water-Soluble and Citrate-Insoluble P_2O_5 of Ammoniated Superphosphates by Official Method

Sample	NH_3	Total P_2O_5	Water-Soluble P_2O_5	Citrate-Soluble P_2O_5	Available P_2O_5	Citrate-Insoluble P_2O_5
	%	%	%	%	%	%
1[a]	0.000	24.52	16.76	6.73	23.49	1.03
2[b]	0.729	24.55	11.90	11.83	23.73	0.82
3[b]	1.496	24.46	11.55	11.76	23.31	1.15
4[b]	2.601	23.51	10.63	11.39	22.02	1.49
5[b]	3.706	23.23	11.89	7.29	19.18	4.05
6[b]	5.024	22.83	8.93	5.73	14.66	8.17
7[b]	6.171	22.54	6.17	6.83	13.00	9.54
8[b]	7.276	22.29	3.55	8.21	11.76	10.53
9[c]	0.731	23.38	14.29	7.45	21.74	1.64
10[c]	1.377	22.81	13.04	7.77	20.81	2.00
11[c]	2.363	22.83	10.68	8.20	18.88	3.96
12[c]	4.046	21.70	8.25	7.19	15.44	6.26
13[c]	5.027	21.33	6.29	7.09	13.38	7.95
14[c]	5.974	21.81	5.69	7.65	13.34	8.48
15[c]	6.994	21.48	5.30	6.45	11.75	9.73

[a] Not ammoniated.
[b] Ammoniated by addition of aqueous ammonia to superphosphate.
[c] Ammoniated by passing ammonia gas into superphosphate.

Table II—Effect of Varying the Weights of Sample in Determination of Water-Soluble and Citrate-Insoluble P_2O_5

Sample	Water-Soluble P_2O_5					Citrate-Insoluble P_2O_5				
	Weight sample used (grams)					Weight sample used (grams)				
	2.0	1.0	0.5	0.2	0.1	2.0	1.0	0.5	0.2	0.1
	%	%	%	%	%	%	%	%	%	%
1	16.76				17.96	1.03				0.63
2	11.90	12.87	13.05	13.52	14.72	0.82	0.93	0.68	0.80	0.54
3	11.55	12.11	12.36	13.39	14.25	1.15	1.23	0.89	1.07	0.69
4	10.63	10.64	11.02	11.88	12.78	1.49	1.74	1.22	1.51	0.69
5	11.89	11.70	12.21	12.72	13.49	4.05	2.60	1.47	1.41	0.81
6	8.93	9.00	9.24	9.81	9.98	8.17	4.57	2.09	1.58	0.86
7	6.17	6.17	6.40	6.85	7.49	9.54	4.40	2.19	1.27	0.83
8	3.55	3.63	3.82	4.53	4 99	10.53	5.31	3.28	1.92	1.05

[1] Received April 15, 1931. Presented before the Division of Agricultural and Food Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Effect of Removal of Soluble Calcium during Digestion with Citrate Solution—From the above facts it would appear that solubility in citrate solution may involve a reversible reaction which may be thought of as a double decomposition of water-insoluble calcium phosphates and ammonium citrate producing soluble calcium citrate and ammonium phosphates. Accumulation of calcium citrate tends to retard the reaction until it attains a state of equilibrium.

Table III—Effect of Varying the Weights of Sample in Determination of Available P_2O_5

Sample	NH_3	Available P_2O_5 as Per Cent of Total P_2O_5				
		Weight sample used (grams)				
		2.0	1.0	0.5	0.2	0.1
	%	%	%	%	%	%
1	0.00	95.8				97.6
2	0.73	96.7	96.2	97.2	96.8	97.7
3	1.50	95.3	95.0	96.4	95.6	97.0
4	2.60	93.7	92.6	90.6	93.6	97.0
5	3.71	82.6	88.8	93.7	93.9	96.4
6	5.02	64.2	80.0	90.8	93.1	96.2
7	6.17	57.7	80.5	90.3	94.4	96.4
8	7.28	52.8	76.2	85.3	91.4	95.4

An attempt was made to remove the soluble calcium by adding ammonium oxalate to the citrate solution. The results are shown in Table IV. The removal of soluble calcium apparently permitted the reaction to proceed to approximate completion, with effects similar to those from the use of small-size samples. It is noticed that using a 2-gram sample in 100 cc. of citrate solution plus 4 grams of ammonium oxalate, and digesting for 30-minute and 2-hour periods, gave approximately the same percentages of citrate-insoluble P_2O_5 as with the use of 0.5- and 0.2-gram samples, respectively, in 100 cc. of citrate solution with 30-minute digestion. Using 4 grams of ammonium oxalate to 100 cc. of citrate solution and extending the digestion to 4 hours gave still less citrate-insoluble P_2O_5.

Table IV—Comparison of Effects on Citrate-Insoluble P_2O_5 of Varying the Weights of Sample and of Addition of Ammonium Oxalate to Citrate Solution

Sample	NH_3	Citrate-Insoluble P_2O_5 by Official Method except for Varying Weights of Sample					Citrate-Insoluble P_2O_5 by Official Method except for Modifying Time of Digestion and Addition of Ammonium Oxalate[a]		
		Weight sample used (grams)					Time (hours)		
		2.0	1.0	0.5	0.2	0.1	1/2	2	4
		%	%	%	%	%	%	%	%
1	0.00	1.03				0.63	1.03		0.92
2	0.73	0.82	0.93	0.68	0.80	0.54	1.25	0.97	0.93
3	1.50	1.15	1.23	0.89	1.07	0.69	1.55	1.23	1.16
4	2.60	1.49	1.74	1.22	1.51	0.69	1.92	1.41	1.29
5	3.71	4.05	2.60	1.47	1.41	0.81	2.37	1.42	1.26
6	5.02	8.17	4.57	2.09	1.58	0.86	3.97	1.85	1.39
7	6.17	9.54	4.40	2.19	1.27	0.83	2.80	1.56	1.35
8	7.28	10.53	5.31	3.28	1.92	1.05	3.30	1.84	1.65

[a] Ammonium oxalate added, 4 grams.

Effect of Addition of Various Amounts of Ammonium Oxalate to Citrate Solution—Determinations of citrate-insoluble P_2O_5 were made using increasing amounts of ammonium oxalate, from 1 to 10 grams for 100 cc. of citrate solution, employing a 2-gram sample, and limiting the time of digestion to 30 minutes.[2] The citrate-insoluble P_2O_5, as shown in Table V, showed no decrease through the addition of ammonium oxalate with materials containing less than 2.6 per cent of ammonia. All samples containing more than this amount of ammonia showed decided decrease in citrate-insoluble P_2O_5 when ammonium oxalate was added to the citrate solution, these decreases being progressively larger as the amount of ammonium oxalate was increased from 1 to 10 grams.

[2] It was observed that 1 gram of ammonium oxalate is soluble in 100 cc. of citrate solution in the cold, whereas 2 grams are partly insoluble in the cold, but all soluble at 65° C. All crystals of ammonium oxalate disappeared after digestion with the sample in the citrate solution for 30 minutes, excepting when 10 grams of ammonium oxalate were used. In this case a few large crystals remained undissolved. These dissolved in the first wash water.

Table V—Effect of Addition of Varying Weights of Ammonium Oxalate to Citrate Solution of Citrate-Insoluble P_2O_5

Sample	Citrate-Insoluble P_2O_5						
	Weight of ammonium oxalate added (grams)[a]						
	None	1	2	3	4	6	10
	%	%	%	%	%	%	%
1	1.03	1.20	1.26	1.09	1.03	1.10	0.96
2	0.82	1.17	1.31	1.25	1.25	1.39	1.51
3	1.15	1.44	1.61	1.28	1.55	1.70	1.67
4	1.49	1.95	2.28	2.17	1.92	1.81	1.62
5	4.05	2.57	3.37	2.68	2.36	1.88	1.59
6	8.17	5.56	6.10	5.01	3.97	2.83	1.93
7	9.54	6.58	5.96	4.72	2.80	1.86	1.14
8	10.53	7.01	5.89	5.49	3.36	2.29	1.68

[a] Ammonium oxalate added to 100 cc. citrate solution; time of digestion, 30 minutes.

Effect of Adding Ammonium Oxalate to Citrate Solution upon Solubility of Rock Phosphate and Tricalcium Phosphate—The rock phosphate used was Superfine Ruhm phosphate and the tricalcium phosphate was Baker and Adamson's c. p. quality. From the results presented in Table VII it is observed that adding ammonium oxalate to the citrate solution markedly reduced the amount of insoluble P_2O_5 of tricalcium phosphate, but had practically no effect on the solubility of the P_2O_5 of the rock phosphate.

Table VI—Effect of Supplying Ammoniated Superphosphates to Buckwheat and Barley in Pot Culture upon Yield and Phosphoric Acid Recovery[a]

Ammonia in Superphosphate	Buckwheat			Barley		
	Dry weight	Content of P_2O_5		Dry weight	Content of P_2O_5	
%	*Grams*	%	*Mg.*	*Grams*	%	*Mg.*
0	13.24	0.95	124	2.18	0.53	11.5
0.729	13.97	0.93	128	3.26	0.51	16.0
1.496	13.65	1.01	138	2.83	0.54	14.8
2.601	14.15	0.98	138	3.07	0.50	14.9
3.706	13.04	0.96	126	2.69	0.51	13.5
5.024	14.30	0.89	128	2.22	0.47	10.3
6.171	13.60	0.88	120	2.81	0.49	13.4
Unfertilized	6.89	0.68	46	1.00	0.41	4.4

[a] Averages of six cultures for each treatment, three employing unlimed acid Wooster silt loam, and three limed Wooster silt loam. Nitrogen supplied in all cultures made uniform by appropriate additions of NH_4NO_3. P_2O_5 supplied in all cultures equivalent to 500 lbs. of superphosphate per 2,000,000 lbs. of soil.

Availability of P_2O_5 of Ammoniated Superphosphate to Buckwheat and Barley in Pot Culture—Buckwheat and barley were grown in Wooster silt loam in pot culture. Superphosphate and a series of six ammoniated superphosphates varying in ammonia content from 0.73 to 6.17 per cent were applied in such amounts as to carry equivalent quantities of total P_2O_5. The nitrogen supplied in all cultures was made uniform by appropriate additions of ammonium nitrate. Yield of dry matter, percentage content of P_2O_5 in the dry matter, and total removal of P_2O_5 were determined. The data are presented in Table VI. There is no evidence of any significant reduction in the availability of the P_2O_5 of any of the ammoniated superphosphates below that of the superphosphate itself. Instead there appears some evidence of an increased availability of the P_2O_5 in the ammoniated superphosphates of low ammonia content.

Data obtained by use of the tentative official method which provides for the use of the water-insoluble residue from a 1-gram sample and digestion for 1 hour in citrate solution are compared with the results of other methods in Table VIII.

From these data it appears that the tentative official method increases phosphorus solubility appreciably, but the increase

Table VII—Effect of Time of Digestion and Addition of Ammonium Oxalate to Citrate Solution on Citrate-Insoluble P_2O_5 of Tricalcium Phosphate and Rock Phosphate

Sample	Weight of Sample	Total P_2O_5	Water-Soluble P_2O_5	Citrate-Soluble P_2O_5	Available P_2O_5	Citrate-Insoluble P_2O_5	Remarks
	Grams	%	%	%	%	%	
Tricalcium phosphate	2	45.78	0.83	14.44	15.28	30.50	Official method
	2	45.78	0.83	21.08	21.91	23.87	Official method[a]
	2	45.78	0.83	15.30	16.13	29.65	Official method, digested 4 hours
	2	45.78	0.83	23.32	24.15	21.63	Official method, digested 4 hours[a]
Rock phosphate	2	37.03	0.02	4.91	4.93	32.10	Official method
	2	37.03	0.02	4.53	4.55	32.48	Official method[a]
	2	37.03	0.02	4.64	4.66	32.37	Official method, digested 2 hours
	2	37.03	0.02	4.76	4.78	32.25	Official method, digested 2 hours[a]
	2	37.03	0.02	4.23	4.25	32.78	Official method, digested 4 hours
	2	37.03	0.02	4.23	4.25	32.78	Official method, digested 4 hours[a]

[a] 4 grams of ammonium oxalate added.

is not so great as that obtained by using a 0.1-gram sample and $^1/_2$-hour extraction, or a 2-gram sample plus 4 grams of ammonium oxalate and 4-hour extraction.

Table VIII—Comparison of Tentative Official Method with Other Methods

Method	Available P_2O_5							
	Sample number							
	1	2	3	4	5	6	7	8
	%	%	%	%	%	%	%	%
1-gram sample, 1-hour extraction[a]	23.63	23.69	23.38	21.90	20.38	17.90	17.86	17.08
2-gram sample, $^1/_2$-hour extraction[b]	23.49	23.73	23.31	22.02	19.18	14.66	13.00	11.76
0.1-gram sample, $^1/_2$-hour extraction	23.89	24.01	23.77	22.82	22.41	21.97	21.71	21.24
2-gram sample plus 4 grams ammonium oxalate, 4-hour extraction	23.60	23.62	23.30	22.22	21.96	21.44	21.19	20.64

[a] Tentative official method.
[b] Present official method.

Discussion of Results

In the dissolution of water-insoluble calcium phosphates of the ammoniated superphosphates in the ammonium citrate solution, it may be assumed that equilibria are set up between the various ions present (NH_4^+, PO_4^{---}, Ca^{++}, Citrate^{---}) and the undissociated salts corresponding to all possible combinations and in accordance with their several dissociation constants. The solubility product of the ions of the water-insoluble calcium phosphates is apparently too low to permit of their complete solution when 2 grams of sample are employed. Addition of ammonium oxalate, by removing calcium ions as insoluble calcium oxalate, should favor the continued solubility of these materials.

It was observed that addition of ammonium oxalate to the citrate solution increased the citrate-insoluble P_2O_5 slightly when the ammoniation of the samples was less than 2.6 per cent. According to Keenen's analyses and calculations, it appears that the products of the ammoniation reaction up to about this point are mono- and dicalcium phosphates and monoammonium phosphate. Using the official method, these are presumably all soluble in the citrate solution. Apparently, however, the solubility of one or more of these constituents is slightly less in the solution containing both ammonium oxalate and ammonium citrate than in a solution containing only the latter salt.

Comparing the water-insoluble residues from the ammoniated superphosphates with tricalcium phosphate, it is observed that the addition of ammonium oxalate to the citrate solution produces a much larger relative effect upon the former, even when the ammoniation of the superphosphate is at the maximum point of 7.3 per cent ammonia. This behavior indicates that the water-insoluble P_2O_5 of ammoniated superphosphates is not identical with precipitated tricalcium phosphate, but that it is much more soluble than the latter in citrate solution to which ammonium oxalate has been added to remove the soluble calcium.

When ammoniated superphosphates are applied to the soil, plants appear to dispose of the soluble calcium liberated from the relatively insoluble calcium phosphates by absorption, with the result that the solution process continues. Thus under field conditions the solubility of the phosphorus is favored by a process not unlike that resulting from the addition of ammonium oxalate to the citrate solution in the laboratory. This is in agreement with Truog's view (*8*) that plants which can take up abundant calcium can assimilate most phosphorus from relatively insoluble calcium phosphates. It should be added, however, that under field conditions soluble calcium may also be removed by reaction with soluble sulfates and carbonates.

One advantage of the addition of ammonium oxalate to the citrate solution is the saving of time of filtration and washing of the citrate-insoluble residue. This process often requires several hours when highly ammoniated superphosphates are used, but when ammonium oxalate is added to the citrate solution, filtration and washing can be finished in 15 minutes.

Possible Methods for Estimation of Citrate-Insoluble Phosphoric Acid

One of the following modifications of the official method would appear worthy of consideration as being perhaps better adapted to measuring the available P_2O_5 in ammoniated superphosphates.

(1) Applicable to superphosphates and ammoniated superphosphates. Follow the official method except for the addition of 4 grams of ammonium oxalate to the 100-cc. portion of citrate solution, and digest either 2 or 4 hours instead of 30 minutes.

(2) Follow present official method for all superphosphates and ammoniated superphosphate samples which contain less than 2.5 per cent of ammonia. For ammoniated samples which contain over 2.5 per cent ammonia, add 10 grams of crystalline ammonium oxalate to 100 cc. of citrate solution and digest for 30 minutes at 65° C. It is recognized that this method would be difficult to apply in practice.

(3) Follow the official method except for the use of a 0.1- or 0.2-gram sample instead of 2 grams.

Literature Cited

(1) Assocn. Official Agr. Chem., Methods, p. 4, 1925.
(2) Assocn. Official Agr. Chem., Corrections of Methods, *J. Assocn. Official Agr. Chem.*, **14**, 71 (1931).
(3) Buie, *Phosphorus Digest*, 2–6, Feb., 1931.
(4) Howes and Jacobs, Ind. Eng. Chem., Anal. Ed., **3**, 70–2 (1931).
(5) Jacob, Hill, Ross, and Rader, Ind. Eng. Chem., **22**, 1385–92 (1930).
(6) Keenen, *Ibid.*, **22**, 1378–82 (1930).
(7) Ross and Jacob, Paper presented at the meeting of the Assocn. Official Agr. Chem., Washington, D. C., October, 1930.
(8) Truog, Wis. Agr. Expt. Sta., *Res. Bull.* **41**, 48 (1916).

Determination of Dextrose and Levulose in Honey by Use of Iodine-Oxidation Method[1,2]

R. E. Lothrop and R. L. Holmes

Bureau of Chemistry and Soils, Washington, D. C.

A study has been made of the effect of a number of factors governing the oxidation by alkaline iodine solutions of dextrose, levulose, and sucrose, such as time, temperature, concentration, and rate of addition of reagents, etc., and a modification of the method for determining dextrose and levulose in honey based on the selective oxidation of dextrose is proposed. Under the given conditions, levulose and sucrose are oxidized only to a very limited extent. The slight oxidation of levulose is apparently due largely to the Lobry de Bruyn rearrangement, and it has been shown to be influenced by time and temperature to a considerable extent. The degree of oxidation of sucrose is small and is not influenced by time to any extent.

Results of determination of dextrose and levulose in a considerable number of honeys by the proposed iodimetric method indicate that levulose is preponderant in normal floral honey, values for the levulose-dextrose ratio ranging from 1.02 to 1.70. Results obtained by this method and the high- and low-temperature polarization method show comparatively close agreement.

THE factors governing crystallization of honey are not thoroughly understood, but it is well known that certain floral types, such as tupelo and sage, remain liquid for long periods of time, whereas alfalfa and some of the clover honeys soon become solid, owing to formation of dextrose crystals. Browne (*5*) has pointed out that the noncrystallizable tupelo honey is characterized by an abnormally high percentage of levulose.

A better understanding of the factors involved in crystallization of honey is desirable, since crystallization must be reckoned with in the handling and storage of honey. For instance, fermentation frequently results when separation of dextrose in crystalline form increases the proportion of water in the remaining liquid portion, producing conditions more favorable to yeast activity. Crystallization is troublesome when honey which is packed in glass containers remains stored for any considerable period of time, or when honey is mixed with peanut butter and similar substances for use as a spread. In the marketing of honey in solid form, the character of the crystalline mass is of importance, small evenly distributed crystals producing a smooth, creamy product suitable for spreading or for filling for layer cakes, etc., whereas coarse granulation produces a product unsuitable for such purposes. Casual observation of a number of samples of granulated honeys will impress one with the great variety of the crystals as regards size and distribution, adhesiveness of the crystallized masses, etc., no two samples possessing exactly the same character.

With a view to obtaining information that would be of value in dealing with problems of granulation, a study of some of the factors governing crystallization of honey has been undertaken. In this connection a simple and accurate method for determining dextrose and levulose in honey is desirable, since the difference in tendency of honeys of different types to crystallize is undoubtedly dependent to a considerable extent upon the ratio in which these two sugars occur. Methods of determining dextrose and levulose in the presence of each other as they occur in honey are of two types: polariscopic (especially high- and low-temperature polarization), and the so-called chemical methods, depending on the selective oxidation or destruction of one sugar in the presence of the other. A selective reduction method for levulose has been developed by Nyns (*22*), and modifications of the iodimetric method have been used by Auerbach and Bodländer (*1*) and others to determine dextrose in honey.

During the past few years considerable work has been done on the iodimetric determination of aldose sugars, especially dextrose. Such methods require only the most commonplace equipment and can be carried out when more elaborate polariscopic equipment is not available. Romijn (*23*) first used iodine in alkaline solution for determining aldehydes. He found quantitative oxidation of aldehydes to acids according to the equation

$$I_2 + 3NaOH + RCHO \longrightarrow RCOONa + 2NaI + 2H_2O$$

He also applied the method to estimating aldose sugars. Willstätter and Schudel (*29*) also have reported that under suitable conditions dextrose is oxidized quantitatively to gluconic acid by iodine in alkaline solution, whereas fructose and sucrose are not affected. Judd (*16*), however, reported incomplete oxidation of dextrose under the conditions of Willstätter and Schudel's experiments, and also found levulose to be oxidized to a considerable extent. Other workers (*1–30*) have reported on the effect of time, temperature, concentration of iodine and sugar, rate of addition of alkali, and other factors involved in the oxidation, and although generally quantitative oxidation of the aldose sugars is shown to take place under certain conditions, there is considerable conflict regarding the influence of the various factors involved, as well as the extent to which sugars other than those containing a free aldehyde group, such as levulose and sucrose, are oxidized.

Auerbach and Bodländer (*1*) applied the iodimetric method to the estimation of dextrose in honey, and calculated levulose from the difference between total reducing sugars (determined by copper-reduction methods) and dextrose. They found that levulose was always preponderant in genuine honey, and fixed the dextrose-levulose ratio at from 1:1.06 to 1:1.19, although higher ratios were found for honeys that had been stored for some time. They used these values for distinguishing between genuine and sophisticated honeys. Gronover and Wohnlich (*14*) using Auerbach and Bodländer's method to determine the levulose-dextrose ratio of a number of genuine honeys, reported that the ratios determined by Auerbach and Bodländer were too high for levulose, some genuine samples showing a preponderance of dextrose. Fiehe (*12*) determined the dextrose-levulose ratios for approximately 50 samples of German honeys, using Auerbach and Bodländer's method, and found dextrose preponderant in more than 70 per cent of the samples examined. These conflicting results leave some doubt as to the reliability of the methods used.

[1] Received April 25, 1931. Presented before the Division of Sugar Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Contribution 108, Carbohydrate Division, Bureau of Chemistry and Soils.

Since the results of different investigators vary so widely as regards the conditions for quantitative oxidation of dextrose, and the extent to which sucrose and levulose are oxidized, a study was first made of some of the methods described by other workers in order to determine, if possible, the reasons for such discrepancies. In addition, a careful study of the oxidation of dextrose, levulose, and sucrose under various conditions and mixed in various proportions has been made in order to devise a more satisfactory method for determination of these sugars as they occur in honey, based on oxidation of dextrose by alkaline iodine. Carefully prepared samples of these sugars were used for this purpose.

Experimental Procedure

Materials Used—The dextrose used had the following analysis: moisture 0.03 per cent, ash 0.02 per cent, and $\alpha_D^{20} = 52.43°$, at a concentration of 6.45 grams per 100 cc.; purity, determined by reduction of Fehling's solution (Munson and Walker method), almost exactly 100 per cent. The levulose used was prepared from 90 per cent levulose (Pfanstiehl brand) by recrystallizing 4 times from alcohol. It had the following analysis: ash 0.16 per cent, moisture 0.28 per cent, and $\alpha_D^{20} = -92.49°$, at a concentration of 9.0778 grams per 100 cc., corrected for ash and moisture. Vosburg's (*28*) rotation for levulose at this concentration and temperature is $-92.75°$. Reducing power as determined by Munson and Walker's method was 0.9234, compared with that of dextrose. Soxhlet (*26*) gives the ratio for reducing power as 0.924. The thiosulfate used was standardized against c. p. potassium dichromate that had been twice recrystallized. The potassium iodide used had been recrystallized and gave no test for iodates.

Auerbach and Bodländer Method (*1*)—This method employs a mixture of equal volumes of 0.2 *M* sodium carbonate and sodium acid carbonate as an alkaline medium with 0.1 *N* iodine, and allows $1^1/_2$ to 2 hours to elapse for completion of the oxidation. With solutions of pure dextrose under the conditions stated in this method (2-hour periods of standing used) oxidation was not complete, although results as high as 99 per cent were obtained. Schuette (*24*) found that 3 to 4 hours were required to complete the oxidation of dextrose by this method. It would seem that the long time necessary for completion of the oxidation is objectionable, both from the standpoint of convenience and the chance of loss of iodine by volatilization, or to slow reactions of iodine with non-sugar substances in the honey. By the use of sodium hydroxide in place of the sodium carbonate–sodium acid carbonate mixture this long period of standing is avoided. It was also found difficult to secure good check results on duplicate analyses when this method was applied to several honey samples. No such difficulty was encountered when using sodium hydroxide and a shorter period of standing.

Slater and Acree's Method—Slater and Acree (*25*) use the quantity of acid formed (as a result of the oxidation of the aldose sugar to acid), as well as the quantity of iodine consumed, as a measure of the degree of oxidation of the sugar. They report that the quantity of excess alkali (sodium hydroxide) used is one of the chief factors controlling the oxidation, and give figures showing a large over-oxidation of dextrose, as well as considerable oxidation of levulose (as much as 37 per cent) and sucrose when amounts of alkali in any considerable excess of that required for the reaction are used. These results are not in harmony with those of Willstätter and Schudel (*29*), Hinton and Macara (*15*), and others.

These authors attempted to avoid the error due to excessive amounts of reagents by carefully controlling the excess of iodine and alkali used, and recommended titrating the excess iodine, partly at least, while the solution is still alkaline. It has been shown by Chapin (*9*) that large errors are introduced when iodine is titrated by thiosulfate in an alkaline solution, as a result of the reactions that take place between the tetrathionate formed and the alkali present, which ultimately involve loss of iodine. Mellor (*21*) gives the following reaction as taking place between tetrathionate and sodium hydroxide:

$$2Na_2S_4O_6 + 6NaOH \longrightarrow 3Na_2S_2O_3 + 2Na_2SO_3 + 3H_2O$$

Since both the sodium thiosulfate and sodium sulfite formed in this reaction will reduce iodine, loss of iodine in this manner will cause the oxidation values for a sugar to appear higher than they actually are. This would explain their reported over-oxidation of dextrose with increasing excess of alkali, and the large apparent percentage oxidation of levulose and sucrose.

By Slater and Acree's recommended method (very small excess of sodium hydroxide and iodine solutions were maintained) with pure dextrose solutions, complete oxidation was not obtained; values from 94 to 97 per cent oxidation resulted over periods of from 5 to 40 minutes. Titration of excess iodine was not carried out as recommended by them, as errors are introduced by titrating iodine with thiosulfate solution in the presence of alkali, but the entire content was made distinctly acid before addition of thiosulfate.

In order to determine the loss of iodine and sodium hydroxide resulting from alternate additions of acid and thiosulfate to an alkaline iodine solution, 20-cc. portions of 0.1 *N* iodine were treated with varying amounts of sodium hydroxide solution, and the iodine was titrated by adding acid and thiosulfate alternately until no more iodine was liberated. Table I gives the results. It will be seen that there is a considerable loss of iodine and sodium hydroxide, even in the total absence of a reducing sugar, and the ratio of iodine to sodium hydroxide consumed is nearly constant at 0.690. This value agrees approximately with the theoretical ratio 0.7 calculated from the equation

$$Na_2S_4O_6 + 20NaOH + 7I_2 \longrightarrow 4Na_2SO_4 + 14NaI + 10H_2O$$

which represents the reaction that takes place between tetrathionate, iodine, and sodium hydroxide, and is very nearly the same as the value 2/3 representing the ratio in which iodine and sodium hydroxide are used up in the oxidation of an aldose sugar by alkaline iodine solution.

Table I—Titration of Iodine in Alkaline Solution by Alternate Addition of Acid and Thiosulfate

(All solutions 0.1 *N*)

Amount Used		Amount Consumed		Ratio Iodine : Sodium Hydroxide Consumed
Sodium hydroxide	Iodine	Sodium hydroxide	Iodine	
Cc.	*Cc.*	*Cc.*	*Cc.*	
10	20	2.70	1.68	0.622
15	20	4.58	3.20	0.698
20	20	6.60	4.55	0.689
20	20	7.40	5.10	0.689
20	20	12.00	8.29	0.691
20	20	9.60	6.64	0.693
20	20	7.74	5.25	0.678
20	20	9.70	6.72	0.692
			Av. ratio[a]	0.690

[a] Excluding No. 1.

The reason for the fairly close agreement shown by values for percentage oxidation of a sugar when the calculations are based either on iodine or sodium hydroxide used up (given by Slater and Acree) lies in the fact that the values for the two ratios are so nearly the same. However, consistently higher results are obtained when the degree of oxidation is based on iodine consumed, which is to be expected, since a slightly greater proportion of iodine is consumed in reactions of iodine and sodium hydroxide involving tetrathionate than is used in reactions involving oxidations of aldose sugars. With 0.08 gram of levulose, 40 cc. and 25 cc., respectively, of 0.05 *N* iodine and 0.1 *N* sodium hydroxide solutions, and the same period of standing (15 minutes), an apparent oxidation value

of 27.47 per cent for the levulose was obtained when acid and the thiosulfate solutions were added alternately in back titration, whereas an oxidation value of only 2.70 per cent resulted when the solution was first made distinctly acid before titration with thiosulfate.

These results show the large errors caused by titrating iodine in alkaline solution, and indicate that the large over-oxidation of aldose sugars and the comparatively high oxidation of levulose and sucrose reported by Slater and Acree[3] are due in large measure to the method of back titration. Large over-oxidation of dextrose or any considerable oxidation of levulose or sucrose has not been found when reasonably large excesses of iodine and sodium hydroxide are present.

Oxidation of Dextrose by Alkaline Iodine

Hinton and Macara (*15*) found that dextrose could be oxidized quantitatively by addition of slightly more than twice the required amount of iodine and sufficient sodium hydroxide solution to combine with the acid formed, and with the excess iodine. By applying these conditions to pure dextrose, the results shown in Table II were obtained. Each titration was carried out on a different day. It appears from these results that 100 per cent oxidation of dextrose is readily obtained under the conditions of Hinton and Macara's experiments.

Table II—Oxidation of Dextrose by Alkaline Iodine
(Temp., approx. 25° C. (room); time of standing, 10 minutes)

Iodine Used	Thiosulfate Equiv. of Iodine	Sodium Hydroxide[a]	Dextrose	Thiosulfate	Iodine Reduced	Oxidation
Cc.	*Cc.*	*Cc.*	*Gram*	*Cc.*	*Cc.*	%
20	20.20[a]	25	0.1000	9.12[a]	11.08[a]	99.82
40	39.52[b]	25	0.0753	22.85[b]	16.67[b]	99.72
40	40.10[b]	25	0.0762	23.17[b]	16.93[b]	99.98
40	40.18[b]	25	0.0754	23.39[b]	16.79[b]	100.29

[a] 0.1 *N*.
[b] 0.05 *N*.

Effect of Temperature on Oxidation of Dextrose and Levulose

For the oxidation of levulose it was found that temperature is an important factor, a change of temperature from 4° to 30° C. causing the percentage oxidation to increase fifteenfold. The results given in Table III show the effect of temperature on the degree of oxidation of dextrose and levulose. It is seen that whereas levulose is influenced considerably by temperature changes, dextrose is not materially affected.

Table III—Effect of Temperature on Oxidation of Dextrose and Levulose

Temp.	Iodine Used[b]	Sodium Hydroxide[a]	Dextrose	Thiosulfate[b]	Iodine Reduced[b]	Oxidation
° *C.*	*Cc.*	*Cc.*	*Gram*	*Cc.*	*Cc.*	%
			DEXTROSE			
4	40	25	0.0747	23.02	16.59	99.45
15	40	25	0.0746	22.98	16.54	99.79
20	40	25	0.0745	22.99	16.53	99.82
30	40	25	0.0744	22.81	16.71	101.10[c]
			LEVULOSE[d]			
			Thiosulfate Equiv. 20 cc. Iodine[e]			
			Cc.			
4	20	12.5	19.86	19.80	0.06	0.35
15	20	12.5	19.80	19.65	0.15	0.89
22	20	12.5	19.80	19.50	0.30	1.78
30	20	12.5	19.74	18.93	0.81	4.81[c]

[a] 0.1 *N*.
[b] 0.05 *N*.
[c] At 30° C. slight loss of iodine due to volatilization probable.
[d] 0.0758 gram levulose for each titration.
[e] Corrected for temperature.

Effect of Time on Oxidation of Dextrose, Levulose, and Sucrose

The results given in Tables IV, V, and VI show the effect of time on the degree of oxidation of dextrose, levulose, sucrose, and mixtures of approximately equal proportions of dextrose and levulose. It is seen from these results that dextrose is oxidized very rapidly, 5 minutes being sufficient for quantitative oxidation, and that longer periods of time (up to 30 minutes) do not increase the oxidation beyond that point. For levulose, however, the oxidation proceeds slowly and at an almost uniform rate for periods up to 30 minutes. The oxidation of a mixture of the two sugars proceeds approximately the same as when they are oxidized singly, except that the oxidation of levulose is inhibited slightly by the presence of dextrose. Sucrose, on the other hand, is oxidized only very slightly by alkaline iodine solutions, and does not show any appreciable increase of oxidation with time, such as is shown by levulose.

[3] Since completion of this work, an article by Kline and Acree (*17*) has appeared, pointing out the error due to the method of titration used by Slater and Acree mentioned above.

Table IV—Effect of Time on Oxidation of Dextrose and of Levulose
(Wt. dextrose for each titration, 0.0784 gram; wt. levulose, 0.0816 gram; temp., 20° C.)

No.	Time	Iodine Used[b]	Sodium Hydroxide[a]	Thiosulfate[b]	Iodine Reduced[b]	Oxidation
	Minutes	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%
			DEXTROSE			
1	Immediate	40[c]	25	23.15	16.08	92.30
2	5	40[c]	25	21.86	17.37	99.71
3	10	40[c]	25	21.85	17.38	99.76
4	15	40[c]	25	21.82	17.41	99.94
5	20	40[d]	25	22.25	17.40	99.88
6	30	40[d]	25	22.24	17.41	99.94
			LEVULOSE			
1	5	20[f]	12.5	19.60	0.22	1.21
2	10	20[f]	12.5	19.50	0.30	1.78
3[e]	20	20[g]	12.5	19.10	0.72	3.97
4	30	20[f]	12.5	18.95	0.87	4.80

[a] 0.1 *N*.
[b] 0.05 *N*.
[c] 40 cc. iodine ≃ 39.23 cc. 0.05 *N* thiosulfate.
[d] 40 cc. iodine ≃ 39.65 cc. 0.05 *N* thiosulfate.
[e] Sample, 0.0758 gram.
[f] 20 cc. iodine ≃ 19.82 cc. 0.05 *N* thiosulfate.
[g] 20 cc. iodine ≃ 19.80 cc. 0.05 *N* thiosulfate.

Table V—Effect of Time on Oxidation of Dextrose and Levulose Mixed in Approximately Equal Proportions
(Each sample contained 0.0784 gram dextrose, and 0.0816 gram levulose; 40 cc. iodine soln. ≃ 39.71 cc. 0.05 *N* thiosulfate; temp., 20° C.)

Time	Iodine Used[b]	Sodium Hydroxide[a]	Thiosulfate[b]	Iodine Reduced[b]	Oxidation Calcd. as Dextrose	Oxidation of Levulose
Minutes	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
5	40	25	22.19	17.52	100.57	0.56
10	40	25	21.99	17.72	101.72	1.65
20	40	25	21.84	17.87	102.32	2.23
30	40	25	21.70	18.01	103.38	3.25

[a] 0.1 *N*.
[b] 0.05 *N*.

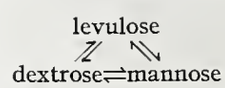
Table VI—Effect of Time on Oxidation of Sucrose
(Each sample contained 0.0750 gram sucrose; temp., 20° C.)

Time	Iodine Used[c]	Sodium Hydroxide[a]	Thiosulfate[b]	Iodine Reduced[b]	Oxidation[d]
Minutes	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%
10	20	12.5	20.23	0.09	0.54
20	20	12.5	20.21	0.11	0.66
30	20	12.5	20.20	0.12	0.72

[a] 0. 1 *N*.
[b] 0.05 *N*.
[c] 20 cc. I_2 sol ≃ 20.32 cc. of 0.05 *N* thiosulfate.
[d] Calculated on basis of 1 mole sucrose to 4 equivalents of iodine.

The results obtained for the influence of time and temperature on the oxidation of the various sugars given above by alkaline iodine are in virtual agreement with those obtained by Hinton and Macara (*15*) who made a somewhat similar study of these sugars.

The fact that oxidation of levulose by alkaline iodine proceeds slowly and at nearly a constant rate over a range of time periods up to 30 minutes, whereas sucrose does not behave in the same manner, might be explained on the basis of levulose undergoing the well-known Lobry de Bruyn rearrangement (*7*), which may be represented by the following equation:



The resulting dextrose and mannose formed as a result of this rearrangement would be readily oxidized. The rate at

which levulose reduces alkaline iodine then would depend on the rate at which the rearrangement takes place and on the rate at which the resulting dextrose and mannose would be oxidized. Since both dextrose and mannose are readily oxidized by alkaline iodine, the rate of oxidation of levulose would depend primarily on the speed of the above-mentioned rearrangement, provided a definite concentration of hypoiodite be maintained to oxidize the dextrose and mannose formed.

The effect of temperature and time on the oxidation of levulose previously pointed out supplies good evidence in support of this view. In this event the percentage oxidation of levulose should be calculated on the basis of 1 molecular equivalent of levulose to 2 equivalents of iodine rather than 1 molecular equivalent of levulose to 4 equivalents of iodine (based on oxidation of a primary alcohol group) as pointed out by Kline and Acree (*17*).

Effect of Rate of Addition of Alkali on Oxidation of Dextrose and Mannose by Alkaline Iodine Solution

A number of oxidation experiments were conducted with mannose to determine whether or not it would undergo quantitative oxidation under the same conditions as dextrose. Under conditions previously determined as yielding 100 per cent oxidation of dextrose, it was found that mannose was oxidized only to the extent of about 80 per cent, even when it was allowed to stand for periods up to 30 minutes. However, 100 per cent oxidation of mannose resulted when the alkali was added slowly. It has been pointed out by Goebel (*13*) and others that the rate of addition of alkali to the iodine-sugar mixture is of considerable importance, rapid addition tending to produce conditions unfavorable for complete oxidation. When alkali is added to a mixture of iodine and aldose sugar, the following reactions are initiated:

$$2NaOH + I_2 \rightleftharpoons NaIO + NaI + H_2O \quad (1)$$
$$NaIO + RCHO + NaOH \longrightarrow RCOONa + NaI + H_2O \quad (2)$$
$$3NaIO \longrightarrow NaIO_3 + 2NaI \quad (3)$$

Too rapid addition of alkali produces iodate formation to such an extent that insufficient hypoiodite remains to oxidize the aldose sugar completely, whereas slower addition of alkali produces hypoiodite at a rate more favorable for complete oxidation of the sugar and less formation of iodate. Table VII gives the results obtained when mannose was treated with alkaline iodine solution. It is seen that quantitative oxidation is obtained only when the reagents are added slowly to the mannose solution.

Table VII—Effect of Rate of Addition of Alkali on the Oxidation of Mannose by Alkaline Iodine Solution

(Each titration involved 0.0750 gram mannose; temp., 20° C.)

No.	Time	Iodine Used[b]	Sodium Hydroxide[a]	Thiosulfate[b]	Iodine Reduced[b]	Oxidation
	Minutes	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*%*
1	10	40	25[c]	27.21	13.44	80.68
2	30	40	25[c]	27.24	13.41	80.50
3	10	40	25[d]	24.10	16.55	99.35
4	30	40	25[d]	23.89	16.76	100.60

[a] 0.1 *N*.
[b] 0.05 *N*.
[c] Added to soln. at once.
[d] Added at constant rate over period of 2 minutes.

With dextrose, quantitative oxidation was obtained whether the sodium hydroxide was added at once or slowly over a period of time. However, when the amount of sodium hydroxide was increased and added at once, there was evidence of incomplete oxidation of dextrose. Table VIII gives the results. It is seen that incomplete oxidation of dextrose results only upon addition at once of a large excess of sodium hydroxide solution. The difference in behavior of dextrose and mannose in this respect apparently is due to differences in their rates of oxidation by alkaline iodine solution.

Since the oxidation of levulose was shown to proceed at an almost uniform rate for periods up to 30 minutes, a study of the oxidation of levulose for longer periods of time was made in order to determine whether or not quantitative oxidation would result after a sufficient period of time had elapsed. A sample containing 0.075 gram of levulose, 40 cc. of 0.05 *N* iodine, and 25 cc. of 0.1 *N* sodium hydroxide showed 8.5 per cent oxidation after 20 hours' standing. This unexpectedly low result was undoubtedly due to the rapid conversion of hypoiodite into iodate, as has been pointed out by Goebel (*13*). Another sample of levulose, when subjected to similar treatment except that the sodium hydroxide was added at the rate of 2 to 3 cc. every 30 minutes, showed 18.92 per cent oxidation at the end of 6 hours. These results indicate that it might be possible to bring about quantitative oxidation of levulose, provided a sufficient concentration of hypoiodite could be maintained over a long period of time. This is rendered difficult because of the rapid formation of iodate from hypoiodite in alkaline iodine solution.

Table VIII—Effect of Rate of Addition of Alkali on Oxidation of Dextrose by Alkaline Iodine Solution

(Time of standing, 10 minutes; temp., 20° C.)

No.	Iodine Used[a]	Sodium Hydroxide[d]	Dextrose	Iodine Reduced[a]	Oxidation
	Cc.	*Cc.*	*Gram*	*Cc.*	*%*
1	40	25[b]	0.0720	15.99	100.03
2	40	25[c]	0.0745	16.53	99.82
3	40	45[b]	0.0720	16.00	100.10
4	40	45[c]	0.0720	15.68	98.09

[a] 0.05 *N*.
[b] Added at constant rate over period of 2 minutes.
[c] Added to soln. at once.
[d] 0.10 *N*.

Application of Iodimetric Method to Determination of Dextrose-Levulose Ratio of Honey

Since a method based on iodimetric determination of dextrose in the presence of levulose (as they occur in honey) would necessitate fixing the conditions of time and temperature for the reaction and correcting for the slight reduction of iodine by levulose under these conditions, the oxidation of dextrose and levulose in varying proportions was studied, time and temperature being fixed at 10 minutes and 20° C., respectively. Results, given in Table IX, show that for a range of dextrose-levulose ratios at least as wide as that encountered in honeys of different types, the oxidation of levulose is fairly constant at approximately 1.2 per cent.

Table IX—Oxidation of Levulose in Presence of Various Proportions of Dextrose

(Temp., 20° C.; time, 10 minutes; 40 cc. iodine = 40.53 cc. 0.05 *N* thiosulfate)

Dextrose	Levulose	Approx. Levulose-Dextrose Ratio	Iodine Used[b]	Sodium Hydroxide[a]	Thiosulfate[b]	Iodine Reduced[b]	Oxidation Calcd. as Dextrose	Oxidation of Levulose
Gram	*Gram*		*Cc.*	*Cc.*	*Cc.*	*Cc.*	*%*	*%*
0	0.0804	..	20	12.5	19.99	0.27	....	1.51
0.0720	0.1608	2.00	40	25.0	24.20	16.33	102.15	1.12
0.0720	0.1206	1.75	40	25.0	24.29	16.24	101.59	1.16
0.0720	0.0804	1.00	40	25.0	24.36	16.17	101.15	1.34
0.0720	0.0603	0.75	40	25.0	24.39	16.14	100.96	1.27
0.0720	0	..	40	25.0	24.60	15.93	100.03	..

[a] 0.1 *N*.
[b] 0.05 *N*.

The dextrose content of different types of honey varies considerably, so that the quantity of sodium hydroxide and iodine remaining unused after the oxidation is complete would also vary, depending on the amount of dextrose present. In order to determine what effect this variation in excess of the reagents might have on the degree of oxidation of dextrose and levulose, experiments were carried out in which the quantities of dextrose and levulose used were kept constant while the amounts of iodine and sodium hydroxide were varied so as to produce variations in the excess quantities of reagents comparing with conditions met in honey analysis. The results,

given in Table X, show that over the range of dextrose content of honeys of different types the degree of oxidation of the two sugars is approximately constant.

Table X—Effect of Variation of Amounts of Iodine and Sodium Hydroxide on Oxidation of Dextrose-Levulose Mixture

(Each sample contained 0.0754 gram dextrose and 0.0741 gram levulose; 40 cc. iodine = 40.18 cc. 0.05 *N* thiosulfate; time, 10 minutes; temp., 20° C.)

Iodine Used[b]	Sodium Hydroxide[a]	Thiosulfate[b]	Iodine Reduced[b]	Oxidation Calcd. as Dextrose
Cc.	*Cc.*	*Cc.*	*Cc.*	%
45	28	28.20	17.00	101.55
40	25	23.19	16.99	101.48
36	22	19.20	16.96	101.31

[a] 0.1 *N*.
[b] 0.05 *N*.

Method

In view of the foregoing results, the following method has been adopted for the analysis of honey: To 20 cc. of a solution containing 0.2 gram of honey in a 250-cc. Erlenmeyer flask, add 40 cc. of 0.05 *N* iodine solution. Run in 25 cc. of 0.1 *N* sodium hydroxide, stopper, and let stand 10 minutes at a temperature of 20° C. Acidify with 5 cc. of 2 *N* sulfuric acid and titrate at once with 0.05 *N* sodium thiosulfate, using starch as an indicator. The weight of dextrose in grams (not corrected for reduction of iodine by levulose) is found by multiplying the cubic centimeters of 0.05 *N* iodine reduced by 0.004502. The total reducing-sugar content of the honey (calculated as dextrose) is determined by Munson and Walker's method, and the per cent dextrose and levulose calculated as follows:

Note—Good agreement was obtained between results for reducing sugars determined by Lane and Eynon's (*19*) volumetric method and the Munson and Walker gravimetric method.

$$\text{Approximate \% levulose} = \frac{\text{\% reducing sugars (calcd. as dextrose)} - \text{\% dextrose (iodimetric method)}}{0.925} \quad (4)$$

$$\text{True \% dextrose} = \text{\% dextrose (iodimetric method)} - 0.012\text{\% levulose} \quad (5)$$

$$\text{True \% levulose} = \frac{\text{\% R. S. (calcd. as dextrose)} - \text{true \% dextrose}}{0.925} \quad (6)$$

$$\text{True \% reducing sugars} = \text{\% dextrose} + \text{\% levulose} \quad (7)$$

In these equations, the factor 0.012 used is taken from Table IX, and represents the reduction of iodine by levulose. The correction as carried out by using the approximate per cent levulose does not give an absolutely correct value, but the difference is small and represents a negligible quantity, well within the experimental error of the method.

The ratio 0.925 used for the relative copper-reducing power of dextrose and levulose was determined by Munson and Walker's method with pure dextrose and levulose at concentrations approximately the same as those used in the method. Browne (*6*) has treated the subject of relative copper-reducing power of dextrose and levulose exhaustively, and gives the ratios determined by several different methods. These values are in rather close agreement with the ratio 0.925, although the ratio varies somewhat depending on the method used for its determination.

The results obtained by applying this method to determining dextrose and levulose in a number of samples of representative honeys[4] are given in Table XI. In every instance the levulose is in excess of dextrose, the levulose-dextrose ratios ranging from 1.02 to 1.70 which is a much greater range than that set by Auerbach and Bodländer (*1*) for German honeys. The average resulting values for levulose and dextrose (39.99 and 33.72, respectively) are approximately the same as those obtained by Browne (*5*) (levulose 40.50, dextrose 34.02) for 92 samples of American honeys in which a method based on high- and low-temperature polarization was used. The levulose content of a number of the samples determined by high- and low-temperature polarization are given in Table XII. The values do not differ materially from results obtained by the iodimetric method, the average difference in values for the two methods being 1.33 per cent.

[4] The honeys used in this investigation were all fresh samples collected during the 1930 season. The importance of using fresh samples in studying the levulose-dextrose ratio of honeys of different floral types is brought out by the findings of Auerbach and Bodländer (*1*) that the proportion of levulose in honey apparently increases on storage.

Table XI—Dextrose and Levulose Content of Honeys of Different Floral Types Determined by Iodimetry

Sample	Predominant Floral Source	Levulose	Dextrose	Ratio Levulose: Dextrose
		%	%	
1184	Buckwheat	37.55	36.74	1.02
1189	Sumac	39.21	32.82	1.19
1195	Dandelion	38.72	35.64	1.09
1200	Honeydew	32.96	29.45	1.12
1201	Catclaw	40.12	35.92	1.12
1202	Chinquapin	41.80	30.20	1.39
1203	Gallberry	41.72	32.70	1.28
1206	Catclaw	39.76	36.50	1.09
1207	Orange	41.03	34.11	1.20
1208	Tarweed	35.91	31.24	1.15
1209	Holly	38.76	31.08	1.25
1210	Manzanita	38.43	34.07	1.13
1213	Eucalyptus	40.58	34.61	1.17
1214	Fruit bloom	38.12	33.60	1.13
1215	Unknown	39.95	29.32	1.36
1216	Tupelo	46.12	27.21	1.70
1228	Honeydew	37.74	33.00	1.14
1229	Sweet clover	39.78	35.40	1.12
1234	White sage	41.69	33.45	1.25
1237	Rosinweed	42.19	38.22	1.08
1239	Alfalfa	38.86	36.51	1.06
1244	Mangrove	41.20	36.19	1.14
1248	Sourwood	43.17	29.70	1.45
1251	Fireweed	39.46	31.54	1.25
1252	White mesquite	41.56	38.01	1.09
1255	Wild flowers	42.20	32.93	1.28
1256	Horsechestnut	42.26	33.31	1.27
1257	Wild flowers	37.82	32.98	1.15
1279	White clover	40.74	36.09	1.13
1285	Fireweed	41.38	32.22	1.28
1287	Bitterweed	37.67	36.58	1.03
1337	Palmetto	40.56	32.95	1.23
1377	Cotton	40.25	38.40	1.05
Av.		39.99	33.72	1.19

Table XII—Comparison of Levulose Content of Honeys Determined by Iodimetry and High- and Low-Temperature Polarization

Sample	Predominant Floral Source	Levulose Iodimetrically	Levulose By polarization
		%	%
1189	Sumac	39.21	36.37
1195	Dandelion	38.72	38.29
1200	Honeydew	32.96	32.43
1201	Catclaw	40.12	39.04
1202	Chinquapin	41.80	40.77
1203	Gallberry	41.72	41.79
1207	Orange	41.03	39.49
1216	Tupelo	46.12	43.06
1229	Sweet clover	39.78	38.00
1239	Alfalfa	38.86	37.81
Av.		40.03	38.70

Further experimentation is now being conducted to determine the influence that substances other than sugars present in honey have on the determination of dextrose and levulose by this method. In view of the close agreement between levulose values obtained by this method and the high- and low-temperature polarization method, it would appear that errors from this source are not excessive.

Acknowledgment

Grateful acknowledgment is made of the valuable suggestions offered by H. S. Paine, chemist in charge of this division, during the course of this work.

Literature Cited

(1) Auerbach and Bodländer, *Z. angew. Chem.*, **36**, 602 (1923); *Z. Nahr. Genussm.*, **47**, 233 (1924).
(2) Baker and Hulton, *Biochem. J.*, **14**, 754 (1920).
(3) Bland and Lloyd, *J. Soc. Chem. Ind.*, **33**, 948 (1914).
(4) Bougault, *Compt. rend.*, **164**, 1008 (1917).
(5) Browne, Bur. Chem., *Bull.* **110** (1908).
(6) Browne, *J. Am. Chem. Soc.*, **28**, 439 (1906); *Intern. Sugar J.*, **23**, 35 (1921).
(7) Bruyn, *Rec. trav. chim.*, **14**, 156 (1895).

(8) Cajori, *J. Biol. Chem.*, **54**, 617 (1922).
(9) Chapin, *J. Am. Chem. Soc.*, **38**, 625 (1916).
(10) Colin and Lievin, *Bull. soc. chim.*, **23**, 403 (1918).
(11) Englis and Byer, Ind. Eng. Chem., Anal. Ed., **2**, 121 (1930).
(12) Fiehe, *Z. Nahr. Genussm.*, **52**, 244 (1926).
(13) Goebel, *J. Biol. Chem.*, **72**, 801 (1927).
(14) Gronover and Wohnlich, *Z. Nahr. Genussm.*, **48**, 405 (1924).
(15) Hinton and Macara, *Analyst*, **49**, 2 (1924).
(16) Judd, *Biochem. J.*, **14**, 255 (1920).
(17) Kline and Acree, Ind. Eng. Chem., Anal. Ed., **2**, 413 (1930); *Bur. Standards J. Res.*, **5**, No. 5, 1060 (1930).
(18) Kolthoff, *Pharm. Weekblad*, **60**, 394 (1923); *Z. Nahr. Genussm.*, **45**, 141 (1923).
(19) Lane and Eynon, *J. Soc. Chem. Ind.*, **42**, 32T (1923).
(20) Levy and Doisy, *J. Biol. Chem.*, **77**, 733 (1928).
(21) Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. X, p. 616, Longmans, Green, 1930.
(22) Nyns, *Bull. assocn. école sup. brasserie Louvain*, **25**, 63 (1925).
(23) Romijn, *Z. anal. Chem.*, **36**, 18 (1897); **36**, 349 (1897).
(24) Schuette, *J. Am. Official Agr. Chem.*, **11**, 164 (1928).
(25) Slater and Acree, Ind. Eng. Chem., Anal. Ed., **2**, 274 (1930).
(26) Soxhlet, *J. prakt. Chem.*, (2) **21**, 227 (1880).
(27) Voorhies and Alvarado, Ind. Eng. Chem., **19**, 848 (1927).
(28) Vosburg, *J. Am. Chem. Soc.*, **42**, 1696 (1920).
(29) Willstätter and Schudel, *Ber.*, **51**, 780 (1918).
(30) Zablinsky, *Z. Ver. deut. Zuckerind.*, **69** (N. S. **56**), 159 (1919).

Impurities in White Sugars

II—Determination of Sulfates, Sulfites, and Aldehyde-Sulfites[1,2]

J. A. Ambler, J. B. Snider, and S. Byall

Bureau of Chemistry and Soils, Washington, D. C.

The quantity of sulfates in white sugars may be accurately determined by direct precipitation with barium chloride from the acidified aqueous solutions of the sugars. By titration of acidified sugar solutions with standard iodine solution both before and after treatment with alkali, the quantities of sulfur dioxide in the sugar as inorganic sulfites and as aldehyde-sulfite addition compounds may be determined. Some sugars contain small quantities of other iodine-absorbing impurities which it is suggested may be polyphenolic.

The sulfate ion is present in the juices of the sugar cane (*22*) and of the sugar beet (*21*) in amounts varying annually and also varying with the type of soil and the climatic conditions. The quantity in the factory juices is further often augmented by sulfates in the lime (*10*, *23*) and the water (*11*) used in the manufacturing processes, and in those factories which use sulfur dioxide, by oxidation of sulfurous acid by the oxygen of the air. Liming and carbonation do not completely remove the sulfates (*19*), a portion of which passes on into the evaporators and vacuum pans where the calcium sulfate frequently contributes to the formation of scale on the heating surfaces. The soluble alkali sulfates, unless their concentration is extremely high, do not separate before graining of sugar and are occluded in the growing sugar crystals.

Determination of Sulfates

The true quantity of sulfates in white sugar cannot be determined from an analysis of the ash of the sugar because during incineration at least a portion of the sulfates is reduced to sulfide by the carbon formed from the sugar, as is shown by the stain of sulfide formed on the dish when the ashing is done in platinum, and by a distinct odor of hydrogen sulfide when the ash is acidified. However, the sulfates may be accurately and easily determined in acidified sugar solutions by precipitation with barium chloride (*9*).

Two series of solutions containing known quantities of potassium sulfate in 200 grams of 50° Brix solutions of cube sugar were prepared and acidified with 5 cc. of concentrated hydrochloric acid. One series was heated to boiling and treated with 10 cc. of 10 per cent barium chloride solution. The other series was treated at room temperature with the same quantity of barium chloride. After the solutions had been thoroughly stirred, they were allowed to stand overnight, the first series on the steam bath, the other at room temperature. The precipitated barium sulfate was collected on tared Gooch crucibles fitted with thick asbestos pads, washed thoroughly with hot water, dried, and heated to 550° C. in a muffle furnace, cooled, and weighed. From the results shown in Table I, it is evident that sucrose does not interfere in the precipitation of the barium sulfate and that there is practically no choice in the two methods. The cold method was adopted for the rest of the work on commercial sugars because of its simplicity and also because it produced only very slight discoloration of the solutions, whereas those which had been heated were badly discolored and turbid from the decomposition of the invert sugar formed by the action of the acid on the sucrose.

Table I—Precipitation of Barium Sulfate in Presence of Sucrose

SO_3 Taken	SO_3 Recovered: Hot precipitation	SO_3 Recovered: Cold precipitation
Gram	*Gram*	*Gram*
0.0049	0.0050	0.0056
0.0099	0.0096	0.0101
0.0493	0.0502	0.0500
0.0986	0.0974	0.0989
0.1972	0.1965	0.1967

For the determination of sulfates in white sugars, 5 cc. of concentrated hydrochloric acid and 10 cc. of 10 per cent barium chloride solution were added to 100 grams of the sugar dissolved in 100 cc. of water. The mixtures were stirred thoroughly and allowed to stand overnight. After the precipitated barium sulfate had been collected and weighed as before, it was calculated to the equivalent weight of SO_3. Some of the results on typical white sugars are recorded in Table II, column 3. The second column gives the percentage of ash in the various sugars as determined by direct charring and incineration at 550° C. While no direct relationship of ash and sulfate content was to be expected, high sulfates generally accompany high ash contents, especially in the beet sugars.

Determination of Sulfites

The presence of sulfites in sugar is attributed solely to the use of sulfur dioxide in the process of manufacture. The methods of determining sulfites in food products, including sugar, have received extensive study in England as a consequence of the establishment by the government (*8*) of a maximum sulfur dioxide content permissible in foodstuffs. The official method finally adopted (*7*, *17*) consists of distillation under prescribed conditions from acid solution in an inert atmosphere and absorption and oxidation of the sulfur dioxide to sulfuric acid, which is determined by titration. Various

[1] Received April 20, 1931.
[2] Contribution 109, Carbohydrate Division, Bureau of Chemistry and Soils.

modifications of two other well-recognized methods are also extensively used, Ripper's method (*20*) of direct titration with iodine (*2, 12, 14*) and Davidsen's qualitative test (*5*) of reduction to hydrogen sulfide as developed quantitatively by Mann (*15*) and others (*3, 18*). These methods were studied comparatively by Spengler and Brendel (*24*), by Jensen (*13*), and by Coghill (*4*), who point out that the iodine-titration method gives results which are to be considered as maxima, owing to the presence in some sugars of other iodine absorbents. The distillation method, as shown by Mason and Walsh (*16*) and by Drake-Law (*6*) is subject to errors due to losses by oxidation by even small amounts of oxygen, and therefore it must be carried out with special precautions and strict attention to technic (*13*).

Table II—Sulfur Trioxide and Sulfur Dioxide in White Sugars

Sugar	Ash	SO_3	SO_2 Inorganic	SO_2 Organic
	%	*P. p. m.*	*P. p. m.*	*P. p. m.*
	DIRECT CONSUMPTION BEET SUGARS			
1	0.017	1.7	56.3	2.5
2	0.014	0.0	10.2	1.2
3	0.028	44.6	10.0	0.0
4	0.021	1.7	9.1	0.5
5	0.019	22.3	38.4	3.1
6	0.034	12.0	58.6	0.4
7	0.254	1188.4	46.1	6.0
8	0.040	104.6	24.3	0.6
9	0.039	29.2	21.0	1.9
10	0.092	270.1	29.4	4.6
11	0.024	13.7	43.4	3.1
12	0.034	20.6	44.2	4.2
13	0.017	0.0	1.1	0.1
14	0.089	360.1	11.8	1.7
15	0.095	356.7	24.1	1.5
16	0.124	471.4	35.9	0.3
17	0.041	145.8	18.0	0.4
18	0.039	10.3	20.2	1.2
19	0.009	0.0	6.1	0.9
20	0.193	872.9	20.8	3.6
	DIRECT CONSUMPTION CANE SUGARS			
21	0.061	294.9	29.9	2.9
22	0.012	24.0	0.9	0.0
23	0.042	44.6	1.3	2.1
24	0.015	19.0	2.2	0.8
	REFINED CANE SUGARS			
25	0.004	0.0	0.6	0.0
26	0.0005	0.0	0.5	0.1
27	0.006	0.0	0.4	0.0
28	0.003	0.0	0.4	0.0
29	0.010	0.0	0.6	0.0

Because of its simplicity of operation, and because it is the only one of the accepted methods by which a partition of the sulfur dioxide into its inorganic and organic aldehydic combinations is possible (*13, 20*), Ripper's original method was chosen as the basis of the determination. One hundred grams of the sugar under examination were dissolved in 125 to 150 cc. of water in an Erlenmeyer flask, and a few cubic centimeters of starch solution were added. The solution was saturated with nitrogen gas to expel the oxygen by bubbling a rapid stream of nitrogen through the liquid for at least 10 minutes. As soon as the stream of nitrogen was stopped, 5 cc. of sulfuric acid (1:3) were added, and the solution was immediately and rapidly titrated with 0.01 *N* iodine solution to an end point which was permanent for at least 2 minutes after four or five rotations of the flask. Blank determinations on the water and reagents were similarly made. The titer of the sugar solution less that of the blank, calculated to SO_2 (1 cc. of 0.01 *N* iodine = 0.32 mg. of SO_2, or, in 100 grams of sample, = 3.2 p. p. m. of SO_2), represents the sulfur dioxide present as sulfurous acid and its salts, and is designated "inorganic SO_2."

For the total SO_2, the same procedure was followed with the exception of the addition of 25 cc. of 1 *N* potassium hydroxide solution to the sugar solution before the saturation with nitrogen, and of the addition of 10 cc. of the sulfuric acid instead of 5 cc. immediately before the titration. The titer so obtained, corrected for the iodine consumption of the reagents as found in a blank determination, and calculated as before, is the "total SO_2." The "organic" or "aldehyde SO_2" is found by subtracting the value of the inorganic SO_2 from that of the total SO_2. The results obtained are tabulated in the fourth and fifth columns of Table II.

In the titration of some sugars, as noted by Spengler and Brendel (*24*), instead of the usual deep blue end point, a fugitive violet one was observed. This is probably due to a small quantity of some interfering substance. In such cases the end point was taken when the violet color lasted at least 2 minutes.

In the refined cane sugars, which, so far as the authors are aware, had not been treated with sulfur dioxide during their manufacture, the small quantity of inorganic SO_2 indicated is, without doubt, not actually SO_2, but rather an iodine-absorbing impurity (*4, 13, 24*). Confirmation of this was indicated by titrating solutions of raw sugars from centrals which are known to use no sulfur dioxide. With these raw sugars very indefinite end points were obtained showing iodine absorbents equivalent to 19, 22, and 32 p. p. m. of SO_2. At present there is no proof as to the identity of these oxidizable substances, but it is suggested that they may be the polyphenols or tannins which are present in cane juice and which have already been shown to be oxygen absorbents (*1*). Such substances are occluded with the other non-sugars in the raw sugar and would be expected to absorb iodine. Their rate of oxidation with oxygen is rapid at first, but slow during the later stages, which is qualitatively similar to the rate of the iodine absorption in the raw sugars as indicated by the fugitive end point. Traces of these polyphenols have been detected in certain raw sugars by measuring the rate of absorption of oxygen by their alkaline solutions (unpublished data). Since at present no stoichiometric relationship between the oxygen or iodine-absorbing powers of these tannins is known, their determination is impossible. Their presence in refined sugar would indicate either that they are not completely eliminated during the refining, or that other polyphenols are formed from the sugar by condensation or rearrangement under the influence of the heat used in the processes of refining.

This interference introduces an error of approximately 1 p. p. m. in the determination of the inorganic SO_2 and the total SO_2, but does not affect the organic SO_2 which is found by difference. Studies of the changes of these types of sulfur dioxide compounds during storage of sugar, and of their effect on the properties of sugar, are now in progress.

Literature Cited

(1) Ambler, Ind. Eng. Chem., **22**, 357 (1930).
(2) Baissac, *Intern. Sugar J.*, **29**, 538 (1927).
(3) Bryan, *Analyst*, **53**, 589 (1928).
(4) Coghill, *S. African Sugar J.*, **14**, 565 (1930).
(5) Davidsen, *Deut. Zuckerind.*, **12**, 939 (1887).
(6) Drake-Law, *Food Manufacture*, **1**, 21 (1927).
(7) Great Britain Ministry of Health, Reports on Public Health and Medical Subjects, No. 43, 1927.
(8) Great Britain Ministry of Health, Statutory Rules and Orders, No. 775, 1925.
(9) Great Western Sugar Co., "Methods of Analysis and Laboratory Control," p. 11, Great Western Sugar Co., Denver, Colo., 1920.
(10) Great Western Sugar Co., *Ibid.*, p. 136.
(11) Great Western Sugar Co., *Ibid.*, p. 144.
(12) Hurst, *Trop. Agr. (Trinidad)*, **4**, 66 (1927).
(13) Jensen, *Food Manufacture*, **1**, 47 (1927).
(14) Jensen, *Analyst*, **53**, 133 (1928).
(15) Mann, *Intern. Sugar J.*, **28**, 647 (1926).
(16) Mason and Walsh, *Analyst*, **53**, 142, 144 (1928).
(17) Monier-Williams, *Ibid.*, **52**, 343, 415 (1927).
(18) Ogilvie, *Intern. Sugar J.*, **28**, 644 (1926).
(19) Pachlopnik, *Z. Zuckerind. cechoslovak. Rep.*, **50**, 269, 281 (1926).
(20) Ripper, *J. prakt. Chem.*, [2], **46**, 428 (1892).
(21) Rümpler, "Die Nichtzuckerstoffe der Rüben," p. 33, Vieweg, Braunschweig, 1898.
(22) Spencer-Meade, "Cane-Sugar Handbook," pp. 11 and 14, Wiley, 1929.
(23) Spencer-Meade, *Ibid.*, p. 396.
(24) Spengler and Brendel, *Z. Ver. deut. Zuckerind.*, **77** (NF64), *Tech. Teil*, 167 (1927).

III—Determination of Labile Organic Sulfur[1,2]

J. A. Ambler

Bureau of Chemistry and Soils, Washington, D. C.

The quantity of the impurities in sugar which contain labile sulfur may be determined by spectrophotometric measurement of the amount of methylene blue produced under definite conditions from the hydrogen sulfide formed during digestion of sugar solutions with alkaline lead acetate. The results obtained indicate that small amounts of compounds containing labile sulfur are present in all types of white direct-consumption sugars. Sucrose, by virtue of its degradation with alkalies, acts as a catalyst for the desulfuring of cystine by alkaline lead solution.

The presence of proteids in the sugar cane and the sugar beet and their juices has long been a matter of common knowledge, and since cystine is a common cleavage product of protein, it is reasonable to suppose that derivatives of this sulfur compound are present in the mill and diffusion juices and possibly in small amounts in the white sugars crystallized from them.

That such is indeed the case was shown qualitatively by boiling with alkaline plumbite solution, thereby taking advantage of the reaction characteristic of cystine and its derivatives in which lead sulfide is formed by degradation. Fifty to 100 grams of a white sugar were dissolved in water, and the sucrose was removed at room temperature as barium sucrate. The excess of barium ions in the filtrate was quantitatively precipitated with sulfuric acid. To the neutral filtrate were added a few cubic centimeters of lead acetate solution and sufficient sodium hydroxide solution to redissolve the lead hydroxide at first formed. This solution was boiled for 1 hour and allowed to cool and stand overnight. In the morning there was a small amount of a finely divided, heavy black precipitate on the bottom of the beaker. Attempts to estimate the quantity of labile sulfur by this simple method failed to yield reliable results.

Because of the extremely small quantity of the organic sulfur compound present and because of the interference of the large quantity of sucrose, it was impossible to detect the presence of organic sulfur by the nitroprusside test (*2*) or by Sullivan's method (*10*), even after desugaring the solutions with barium hydroxide. A modification of the plumbite digestion method combined with the methylene blue colorimetric method for hydrogen sulfide (*1*, *4*, *7*, *8*, *9*) and with spectrophotometric measurement of the methylene blue formed as described in the following paragraphs, proved successful and disclosed the fact that sucrose acts as an accelerator for the formation of lead sulfide in the degradation of cystine.

Apparatus

Since the method consists in part of an alkaline lead acetate digestion, it is essential that no rubber or cork be used to make unions at those points where they will come in contact with hot vapor or liquid. Any all-glass apparatus for reflux digestion of the type of the Zeissel methoxy apparatus, which has provision for introducing a stream of gas and which has a digestion flask of at least 500 cc. capacity, will be satisfactory. An apparatus, cheaper than a Zeissel outfit of the size needed, although more unwieldly because of its rigidity, was made by welding a 500-cc. Pyrex Claissen flask *D*, from which the small side outlet tube had been removed, to a Pyrex condenser, *E*, and sealing in a gas inlet tube as shown in Figure 1. The top of the condenser was closed by a rubber[3] stopper bearing a T-tube, *F*, through which the stem of a dropping funnel, *G*, extended into the condenser. The T-tube was attached to the stem of the dropping funnel by rubber tubing. The other opening of the T-tube was attached by rubber tubing to a glass tube leading to a wash bottle, *H*, which was directly connected to the absorption bottle, *J*, and this to the trap wash bottle, *K*. The gas inlet tube of the digestion flask, *D*, was connected through a series of three wash bottles, *A*, *B*, and *C*, with a tank of compressed nitrogen gas. Bottle *A*, connected directly with the nitrogen tank, contained a solution of potassium permanganate to remove oxidizable impurities in the nitrogen, bottle *B* contained alkaline pyrogallol solution to remove any oxygen, and bottle *C* contained sodium plumbite to remove any trace of hydrogen sulfide.

The wash bottle, *H*, between the condenser and the absorption bottle contained a solution of potassium dihydrogen phosphate to absorb any volatile acids which may be carried over (*7*). The absorption bottle, *J*, contained St. Lorant's zinc acetate solution (*7*). The trap wash bottle, *K*, contained water and served merely to prevent air from backing into the absorption bottle.

Solutions

Cystine Standard—Two-tenths gram of cystine was dissolved in a little 1:4 hydrochloric acid and made up to 100 cc. with distilled water. Five cubic centimeters of this solution were diluted to 500 cc., giving a solution which contained 0.02 mg. of cystine per cubic centimeter.

Lead Solution—A saturated neutral lead acetate solution was used as the lead solution throughout the whole procedure.

Alkali—For the digestion, a 5 per cent suspension of powdered magnesium oxide. For making sodium plumbite, a 30 per cent solution of sodium hydroxide.

Wash Liquids for Nitrogen—(*a*) Two per cent potassium permanganate solution.

(*b*) For alkaline pyrogallol solution, 10 grams of pyrogallol were dissolved in 30 cc. of water, and a solution of 175 grams of sodium hydroxide in 60 cc. of water were added. This solution must be renewed frequently, before it becomes completely exhausted.

(*c*) Alkaline lead acetate solution. To 5 cc. of the saturated lead acetate solution sufficient 30 per cent sodium hydroxide solution was added to redissolve the initial precipitate of lead hydroxide. The solution was then diluted as much as necessary to give a minimum depth of 2 inches (5.08 cm.) of liquid through which the nitrogen must bubble.

Absorbing Solution for Volatile Acids—Fifty cubic centimeters of a 10 per cent solution of potassium dihydrogen phosphate (*7*).

Sucrose Solution for Standards—Twenty grams of cube sugar or of specially purified sucrose were dissolved in water and diluted to 100 cc. with distilled water.

Hydrochloric Acid—One volume of concentrated hydrochloric acid was diluted with four volumes of water.

St. Lorant's Absorption Solution (*7*)—Fifty grams of zinc acetate, 10 grams of sodium acetate, and 0.5 gram of sodium chloride were dissolved in water and diluted to 1 liter.

St. Lorant's Developing Solutions (*7*)—(*a*) One gram of dimethyl-*p*-phenylenediamine sulfate was covered with 100 cc. of water, and immediately, with cooling, 400 cc. of 60° Bé. sulfuric acid were added. With vigorous cooling, the solution was diluted to 2 liters.

(*b*) Twenty-five grams of ferric ammonium sulfate (clear,

[1] Received April 20, 1931.

[2] Contribution 110, Carbohydrate Division, Bureau of Chemistry and Soils.

[3] All rubber stoppers and tubing used were boiled with alkali and then with dilute acid and finally with water before being used.

purple crystals) were moistened with 5 cc. of 60° Bé. sulfuric acid, and immediately dissolved in water and diluted to 200 cc.

Procedure

The digestion apparatus was washed twice with tap water, cleaned with concentrated nitric acid, and rinsed thoroughly twice with tap water and twice with distilled water. This thorough cleaning was done before each determination.

The reagents were introduced through a clean tube inserted into the condenser and extending to a point below that at which the vapors will condense. One cubic centimeter of lead acetate solution was added first, next a measured volume of the standard cystine solution, and then 25 cc. of the magnesia suspension. The liquid adhering to the tube was washed into the flask by rinsing the inside and outside of the

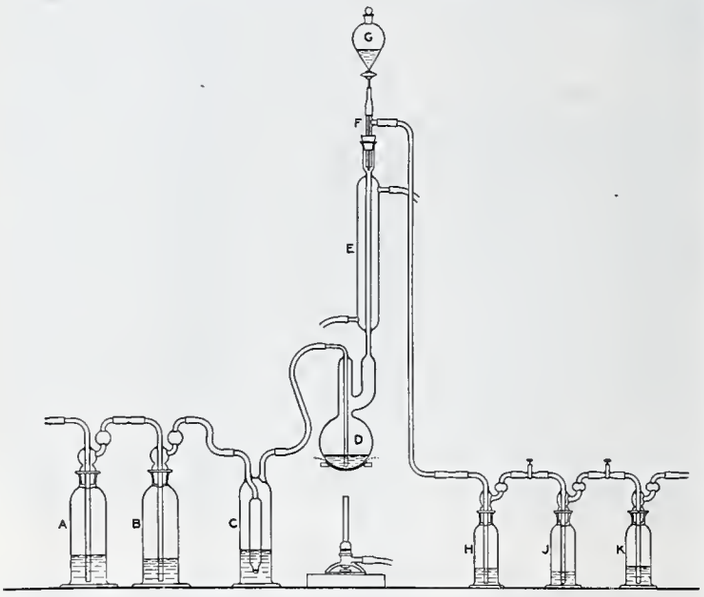


Figure 1—Apparatus for Labile Sulfur in Sugar

tube and the inside of the condenser with a total volume of 125 cc. of distilled water. For the standards containing sucrose, 50 cc. of the 20 per cent (by volume) sucrose solution (10 grams of sucrose) were added through the tube instead of the first portion of the rinse water, and the washing down was completed as before with a total volume of 75 cc. of water. No lead compound must be allowed to remain in the condenser above the highest point washed by condensing vapors.

Determination

Alkaline Digestion—The flask was connected by the inlet tube and the T-tube with the properly charged wash bottles. After 5 cc. of water had been placed in the dropping funnel as a seal, nitrogen was passed through the apparatus until the air was completely displaced from it. While this was taking place, the absorption bottle, *J*, was charged with 20 cc. of St. Lorant's absorption solution and 10 cc. of water and connected to the apparatus together with the trap, *K*. At the same time another absorption bottle was similarly charged and connected to the end of the train of bottles until all the air had been displaced from it, when it was disconnected and immediately closed to the air. Its contents served for the development of the blank standard solution for comparison in the spectrophotometric measurements later.

The stream of nitrogen was slowed down to about one bubble a second, and the mixture in the digestion flask was boiled gently for 2 hours. At the end of this period the stream of nitrogen was speeded up so that there was a steady series of bubbles in the absorption bottle, one bubble leaving the bottom of the inlet tube just as the preceding one was about to break on the surface of the liquid. Without admitting air to the apparatus, 60 cc. of the 1:4 hydrochloric acid were added through the dropping funnel, which was again sealed with about 5 cc. of water. Cracked ice was placed around the absorption bottle and the closed bottle containing the blank. As soon as the magnesia was all washed down from the sides of the flask, heating was stopped and the stream of nitrogen continued for a total of 1 hour from the time of acidification.

Development of Methylene Blue—The absorption flask was disconnected, instantly closed to the air, and removed from the ice bath. With as little opening to the air as possible, 7.5 cc. of St. Lorant's solution of dimethyl-*p*-phenylenediamine and 2 cc. of his ferric sulfate solution were quickly pipetted into the absorption bottle and into the blank bottle. The bottles were closed and shaken. By applying alternately gentle suction and pressure on the inlet tubes with the outlet tubes closed, the insides of the inlet tubes were wet with the mixtures in the bottles. The closed bottles were allowed to stand for 1 hour, during which time they assume room temperature and the maximum depth of color of the methylene blue is developed. The colored solution was then transferred to a graduated cylinder containing 1 cc. of 95 per cent alcohol and diluted with water to 50 cc. After the solution had been thoroughly mixed by pouring it back and forth into the bottle twice, it was filtered through a dry paper. The first few cubic centimeters running through were discarded, and the rest of the clear filtrate was used to fill a 1-dm. color-analyzing tube. The blank solution was treated in exactly the same way and used as the standard in the spectrophotometric determination of the transmittancy, T, of the colored solution at 610 mμ.[4] This method of using as the standard a blank solution containing all the reagents in the same concentrations and under the same conditions, practically corrects the value of T for the transmittancy of the solution due to the reagents. From the value of T, that of $-\log T$ (or $\log 1/T$) was obtained and plotted on coördinate paper against the quantity of cystine taken. By this means regular curves, as shown in Figure 2, were obtained.

In determining the quantity of labile sulfur in a sample of sugar, the sugar was dissolved in distilled water in the proportion of 500 grams of sugar to 375 grams of water, and the solution was passed through a 150-mesh copper screen to remove suspended fibers, hairs, and particles of other foreign matter. After the lead acetate and the magnesia suspension had been added to the digestion flask, 350 grams of this sugar solution (equivalent to 200 grams of sucrose) were introduced to wash the lead-magnesia mixture from the tube and condenser. The latter were finally rinsed down with a little water from a wash bottle. The subsequent procedure was the same as before. If the color developed was too intense to be read accurately in the 1-dm. tube, either the colored solution was diluted to 200 cc. (or more if necessary) instead of to 50 cc., or shorter tubes were used. In either case, the $-\log T$ value so found was multiplied by the appropriate multiple of 50 cc. used, or by the reciprocal of the length of tube used when this length was expressed as fractions of a decimeter. If the color was so intense that the $-\log T$ value was too great to fit on the standard curve, the determination was repeated with less sugar. The quantity of labile organic sulfur expressed as milligrams of cystine was found by means of the curve

[4] Methylene blue has two absorption bands located at 609.3 and 667.8 mμ (Schultz Farbstofftabellen). The former (or in round numbers 610 mμ) was found more convenient than the latter, since it is in a portion of the spectrum where more accurate measurement is possible and may be used for a greater range of concentrations without resorting to dilutions or to shorter tubes.

developed from known quantities of cystine when the determination was made in the presence of sucrose, and calculated to parts per million.

Discussion

Although neither the production of lead sulfide from cystine (*3*, *6*, *9*) nor the formation of methylene blue from hydrogen sulfide (*7*, *8*) is quantitative, it is possible to use these reactions in the estimation of labile sulfur in white sugars, if all conditions of the determination are maintained as strictly uniform as possible, as is shown by the results represented by Figure 2. The deviation of these curves from a straight line is due in part to the fact that the formation of lead sulfide is not quantitative under the conditions of the method, and is

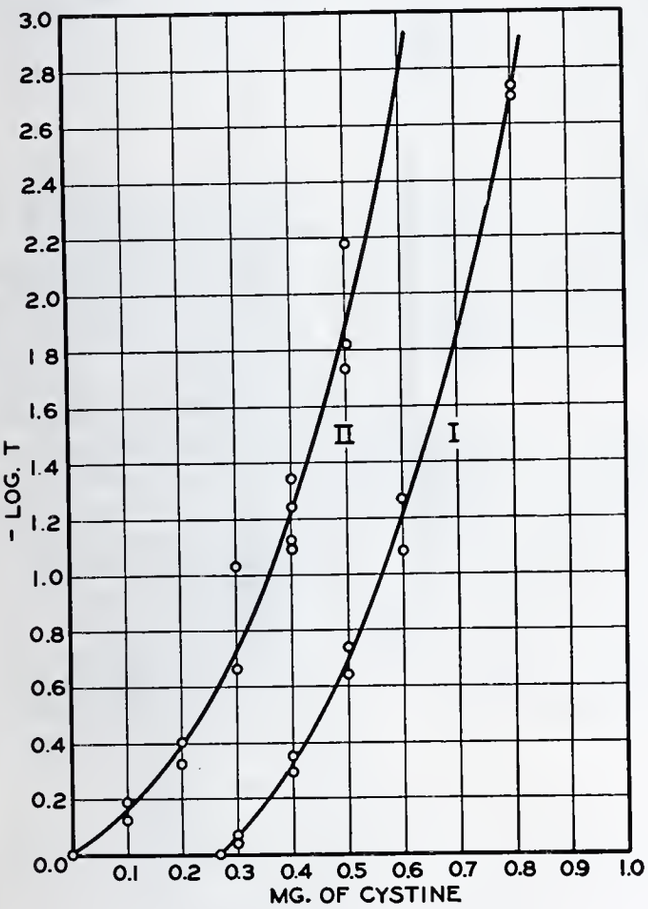


Figure 2—Curves for Determination of Cystine

apparently a function of the original concentration of cystine. Another factor tending to cause deviation from a straight line is to be found in the different quantities of ferric ions in the standard and the colored solutions used for spectrophotometric measurement, since some ferric ions are reduced to colorless ferrous ions in the production of methylene blue. However, while this introduces an error its magnitude is relatively small at 610 mμ and may be wholly ignored, inasmuch as the method involves only relative values based on cystine and obtained by means of a specified arbitrary procedure.

Curve I of Figure 2 shows the results obtained with solutions of cystine and demonstrates the feasibility of the method. Curve II shows the results obtained with solutions of cystine in the presence of sucrose, which increases the sensitivity of the method by accelerating the degradation of the cystine. This observation is in agreement with those reported by Clarke and Inouye (*3*), who found that salicylic aldehyde, benzaldehyde, and pyruvic acid catalyze the desulfurization of cystine. In the case of sucrose, the decomposition products formed by heating the sugar with alkali act in a similar way. Fischler (*5*) has noted that sucrose yields with potassium hydroxide a product (which he asserts is methylglyoxal), which yields iodoform on the addition of iodine solution. Methylglyoxal ($CH_3CO.CHO$) is the aldehyde of pyruvic acid ($CH_3CO.COOH$), and since Clarke and Inouye (*3*) have shown that the catalytic effect of pyruvic acid is to be attributed to the ketonic group, it is to be expected that methylglyoxal, which contains the same ketonic grouping and in addition an aldehydic group, would also act as a catalyst for the splitting off of hydrogen sulfide from cystine. The formation of iodoform from the cleavage products of sucrose when warmed with magnesia suspension was observed during this investigation by adding a solution of potassium iodide and iodine to mixtures of sucrose and magnesia suspension without the addition of sodium hydroxide. This would indicate that the action of magnesia suspension on sucrose is qualitatively similar to that of sodium hydroxide. In the experiments magnesia was used in the alkaline digestion instead of sodium hydroxide, because the solid magnesia in the suspension facilitates quiet boiling without bumping and maintains the pH of the solution more nearly constant than would a solution of a soluble alkali, and also because magnesia suspension is less destructive to the sucrose and causes less discoloration during the 2-hour digestion period.

The method is accurate to within 0.05 mg. of cystine, within the range from 0.1 to 0.6 mg. Because of the steepness of the $-\log T$ curve, a comparatively large difference of $-\log T$ values on duplicate determinations makes very little difference in the results. Below 0.1 mg. of cystine the method is not accurate because of the extremely small amount of methylene blue formed and the resulting paleness and small $-\log T$ value of the solution. Determinations which fall on this portion of the curve are best reported as "traces" or "less than 0.1 mg." The results obtained with representative white sugars are given in Table I, and indicate that all types of white sugars contain some labile organic sulfur compounds. The figures given are the averages of two or more determinations, except as noted.

Table I—Labile Organic Sulfur (as Cystine) in White Sugars

Sample	Amount Found
	P. p. m.
DIRECT-CONSUMPTION BEET SUGARS	
a	0.8
b	1.5
c	1.1
d	0.8
e	0.8
f	1.6
g	2.9
h	Trace
DIRECT-CONSUMPTION CANE SUGARS	
i	3.4
j	0.8[a]
k	0.4[a]
REFINED CANE SUGARS	
l	1.4
m	Trace
n	0.8

[a] Single determinations.

Literature Cited

(1) Almy, *J. Am. Chem. Soc.*, **47**, 1381 (1925).
(2) Blankenstein, *Biochem. Z.*, **218**, 321–30 (1930).
(3) Clarke and Inouye, *J. Biol. Chem.*, **89**, 399 (1930).
(4) Fischer, *Ber.*, **16**, 2234 (1883).
(5) Fischler, *Z. angew. Chem.*, **42**, 682 (1929).
(6) Mörner, *Z. physiol. Chem.*, **34**, 210–2 (1902).
(7) St. Lorant, *Ibid.*, **185**, 245–66 (1929).
(8) St. Lorant, *Ibid.*, **193**, 56–8 (1930).
(9) Sheppard and Hudson, Ind. Eng. Chem., Anal. Ed., **2**, 73–5 (1930).
(10) Sullivan, *U. S. Public Health Repts.* **41**, 1030–56 (1926).

Possibilities of adding millions to the value of the American fisheries industry are seen in the establishment of a new research laboratory of the Bureau of Fisheries at Gloucester, Mass. Officials foresee a further elimination of waste and improvements in fish merchandising which will add considerably to the importance of the industry, already valued at $125,000,000.

A Large-Scale Soxhlet Extractor[1]

S. Allan Lough

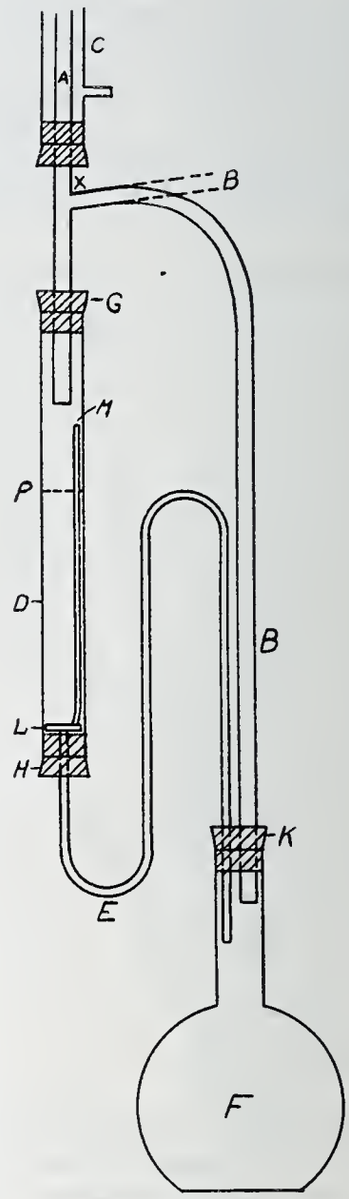
Department of Chemistry, University of Nevada, Reno, Nev.

IN ORDER to obtain large quantities of an oil for analysis, the extractor described herewith was devised. It lends itself readily to adaptation to special problems and can be made from materials found in almost every laboratory.

Near one end of the Pyrex glass tube *A*, of inside diameter 0.8 cm., a similar tube, *B*, was sealed in at *X* at the angle indicated by the dotted lines. This angle prevents excessive refluxing into the flask *F*. The second tube, *B*, was then bent downward in a gentle curve until the lower portion of tube *B* was parallel to tube *A*. The jacket of a Liebig condenser, *C*, fitted with rubber stoppers, was placed on the upper portion of tube *A*. Another condenser jacket was cut off just below the water inlet and the edges were fire-smoothed. The other water inlet was sealed off in a flame. This served as the extraction chamber. The siphon tube, *E*, was an ordinary copper tube of internal diameter 0.3 cm. A 2-liter Florence flask, *F*, was used as a chamber in which to boil the solvent and to collect the extract. The parts were assembled as indicated in the diagram and the whole was mounted, by the use of clamps, on a large ring stand. Corks coated with wet chrome-gelatin (*1*) were used to complete the joints at *H* and *K*. Cork *G* was coated only on its under surface with chrome-gelatin. The chrome-gelatin was allowed to dry for 2 days.

By virtue of the flexibility of the copper tube *E*, chamber *D* was removed from stopper *G* and the material to be extracted was introduced in a long, cloth sack. A ring, *L*, made of glass rod, was laid on stopper *H*. This ring supported the sack of material and prevented the occlusion of the outlet of the siphon. A glass tube, *M*, open at both ends, was placed along the side of chamber *D* to make sure no air would be trapped within ring *L*, thus ensuring drainage of the chamber as soon as the liquid rose to the level *P* or only slightly higher. Siphoning is more complete if the siphon tube is longer and if extra bends are made in any convenient direction. The lower end of tube *A* should be at least 1 cm. below cork *G* to keep solvent off the cork. If flask *F* is of large volume, chamber *D* can be filled many times with fresh material before the solution in *F* becomes too concentrated for longer boiling. If additional solvent is needed, it can be added at the top of tube *A*. If only one charge of material is to be extracted, the siphon tube can be made of glass.

[1] Received April 24, 1931.



A Large-Scale Soxhlet Extractor

Literature Cited

(1) Lassar-Cohn, "Organic Laboratory Methods," translated by Oesper, p. 194, Williams & Wilkins, 1928.

Food Industries Welcome Legal Standards

The food industries are showing a tendency to support legislation for standardization of all manufactured food products and for more extensive legal control of sanitary conditions in food manufacturing plants and establishments where foods are handled and sold, according to P. B. Dunbar, of the Federal Food and Drug Administration. Legislative control of advertising also has been endorsed by several organizations of national scope dealing in foods and drugs, and the industries in many instances are taking steps to control their advertising in the direction of moderation in the claims made. Quoting Doctor Dunbar:

"If I am correct in my estimate of the present attitude of the food industries toward the food law and of the value of the enforcement of the law to the industry, we may expect future developments to be in the direction of affording the consumer even greater guarantees of the integrity and good quality of food products. We may further expect the industry itself to take the steps necessary to bring about such extensions of the law.

"One of the most serious problems we have encountered is the determination of what actually constitutes a violation. The Food and Drugs Act is most general in its language. With one exception, that of butter, there is no legislative standard for food products.

"After analysis, the general terms of the law must be applied to the commodity under consideration and a decision must be reached, first by the Department of Agriculture and later by the courts, as to whether the particular condition constitutes a violation of the law. Food products from a law enforcement standpoint very naturally divide themselves into three groups: first, those which are unmistakably legal; second, those just as definitely illegal. Between these two is a third group in a doubtful zone where the violation is not established so easily and yet where the most serious damage may be done to the consuming public and honest competitors unless abuses are definitely checked."

Analytical Industrial and Engineering Chemistry Edition

Published by the American Chemical Society

Volume 3 OCTOBER 15, 1931 Number 4

Improved Technic for Microgravimetric Analyses[1]

Paul L. Kirk and Roderick Craig

Division of Biochemistry, University of California Medical School, Berkeley, Calif.

An apparatus is described for microgravimetric analyses, such as sulfate, halide, and phosphate determinations, on a very small sample. The technic for use of the apparatus is described. The accuracy is found to be chiefly limited by the possible accuracy of weighing and method of precipitation rather than by the apparatus itself.

Of all the various types of microchemical analyses, those based on determination of the weight of a precipitate seem to offer the greatest technical difficulties. This is largely owing to the necessity of transferring the precipitate quantitatively from a reaction vessel to a filter, an operation in which small losses are very apt to occur. Such losses are of little importance in macroanalyses, but on a micro scale they may represent a large percentage error.

Obviously there is need for a type of apparatus which will combine the reaction vessel with the filter in such a manner that the transfer of precipitate is either eliminated or rendered easy. It is the purpose of the authors to describe in this paper a practical apparatus of this nature and a technic for its use in such determinations as those of sulfate, halide, phosphate, etc., all of which are used constantly in both chemical and biological work.

Description of Apparatus

Figure 1 shows diagrammatically the design of the apparatus. *A*, the reaction chamber, is made from a portion of a test tube attached at the bottom to a heavier tapered tube of smaller diameter, suitable for grinding. In *A* is a rod, *D*, hooked at the top and ground into the tapering end of *A*. The outside of this tapering end is, in turn, ground into the top of filter tube, *B*. About a centimeter from the bottom of this ground connection is a platinum plate made from foil about 0.005 inch (0.127 mm.) in thickness. This plate has several small punched holes of 0.5 mm. or less. It fits tightly inside the tube, and after it is in place it is fused to the inside of the glass tube by use of a fine blast flame. The apparatus can be constructed by a glassblower of moderate skill without any serious difficulty. A second rod, *E*, should be constructed with a hook on the end for removal of the ground rod, *D*, from its seat. The hooks on both rods must be of sufficient strength to withstand a moderate pull, and for this reason, the size of rod in the hook should be drawn down little if any from the size of the remainder of the rod.

Experimental Procedure

In using this type of filter, a few points of technic are important. Dry ground-glass joints nearly always leak a little, and the use of grease in this apparatus is not desirable. Glycerol was found to be a very suitable lubricant since it is infinitely miscible with water and alcohol, but dissolves so slowly that the ground glass connections easily retain it almost indefinitely when the parts are pressed together.

A filter pad of asbestos is necessary. This must be of a very good quality and in a proper state of division. Asbestos prepared as for use in the micro calcium method of Kirk and Schmidt (*2*) is satisfactory. Here a good grade of asbestos washed in acid and ignited was thoroughly dried and ground either in a ball mill, or, more laboriously, by a mortar and pestle, until it was quite fine. If the ground product is suspended in water, the fineness will be found easy to grade by the differential rate of settling.

As used in an ordinary gravimetric analysis, such as sulfate or halide, the procedure is as follows: The disconnected filter tube *B* is placed in a short stopper in a suction flask. Very mild suction may be produced by use of a pinchcock on the rubber tube to the vacuum line. This may be opened slightly from time to time. In order to make the filter mat properly, the flask of asbestos suspension is shaken and a little of it removed with a pipet having a large orifice, and is run into the filter tube. This gives a thin layer of comparatively coarse asbestos which is sucked down firmly. After a few moments, the coarse asbestos in the flask has settled and some of the fine asbestos is removed with the pipet and run on to the filter until a thin but quite tight filter pad is obtained. After the usual washing with water several times, it is washed with a small amount of alcohol delivered from a small pipet, and finally in the same way with a little ether. The tube is withdrawn from the stopper, wiped with a soft cloth, and placed in a copper block to reach equilibrium with respect to moisture and temperature. It is weighed on a microbalance, and then replaced on the suction flask and moistened with a little water which is sucked slowly through. If the filter pad has been properly made and washed, this water will filter through absolutely clear. If it carries through a little asbestos, it should be thoroughly washed as before, redried, and reweighed. This will occasionally save repeating a determination entirely, since loss of any asbestos when filtering practically invalidates the result.

In the meantime, the reaction chamber is prepared for the precipitation. The plug *D* is moistened with glycerol and pressed firmly into its seat in the end of *A*. In working with

[1] Received March 16, 1931.

different sets of apparatus, a curious fact has come to light. With some reaction chambers, it is a simple matter to clean them well enough so that precipitate does not cling to the walls. With others, this is exceptionally difficult. In attempting to avoid having precipitate cling to the walls, the use of acetone in the solution was found to be remarkably efficient. In the analysis of sulfates, for example, the precipitation is carried out as follows: About 0.5 cc. of pure acetone is used to rinse down the sides of the vessel and the rod *D* which has already been inserted. This remains in the vessel. Immediately, a little water and a few drops of dilute hydrochloric acid and finally the sample are added. The sample may be added from a weight buret, a carefully calibrated microburet, or a micropipet. The chamber *A* is then dropped into a cut-off test tube which is of the proper length to just contain it, and with an inside diameter a bit larger than the chamber *A*, and which is immersed in a boiling water bath. When heated sufficiently a few drops of barium chloride solution are added slowly with shaking or twirling between the hands. The tube is replaced in the water bath and heated with occasional twirling until the barium sulfate is completely coagulated. In the presence of acetone, the coagulation of barium sulfate is very complete and rapid, and clinging to the walls is eliminated. With some sets of apparatus it is apparently not necessary to use acetone. The reason for this is still obscure.

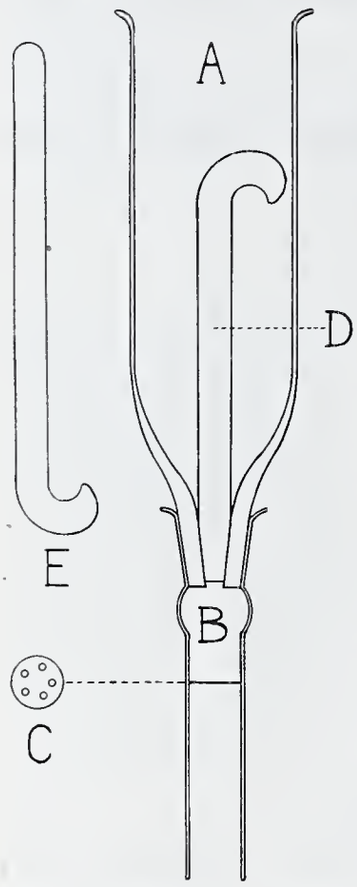


Figure 1—Diagram of Apparatus (Actual Size)

In precipitating halides, less trouble is experienced from clinging to the walls and usually no difficulty is found in making the precipitation directly in the usual way.

When the tube *A* is heated sufficiently it is removed and the ground end is moistened with glycerol and inserted into the end of *B* on the suction flask. The plug is pulled and mild suction applied. The hook *E* which may have some precipitate adhering, is carefully washed off with the wash bottle, and the hook of *D* is hung over the edge of *A*. The precipitate is of small bulk, and consequently a few washings are sufficient. Without allowing the sides of *A* to dry and deposit any dry precipitate, a small pipet full of alcohol is used to rinse down the sides. This immediately stops the climbing of the precipitate and rinses it quantitatively into the filter from the walls, providing only that the walls have previously been well cleaned with chromic acid, and that the precipitate has been properly coagulated and has not been allowed to dry on the walls. When the last of the precipitate has been removed from the walls, *A* is removed from *B* and laid aside. The material on the filter and on the ground portion of *B* is washed further with water and alcohol, and finally with a little ether, to remove all traces of glycerol. The filter is dried as before on a copper block, equilibrated, and weighed. Originally, it was feared that a trace of glycerol might remain after the final washing, and to assure removal of this, the tube was heated in a regenerating block as described by Pregl (*3*, p. 76) to a temperature of about 200° C. This was carried out on both the empty tube and that containing the precipitate. Later this procedure was abandoned since it did not increase the accuracy of the method and required considerably more time.

The filter apparatus has been tested with a number of points in view. Leakage around the ground connections would be serious, but is absolutely eliminated by the use of glycerol. The largest chance for error would seem to be in removal of all the precipitate from the sides of the reaction chamber to the filter. That part of the precipitate which creeps up the sides is very simply washed down by alcohol. The use of acetone in the mixture prevents quite effectively any tight adherence to the walls. No other agent except acetone was found for this purpose, although alcohol and glycerol were both tried. However, if the particular type of precipitate cannot be removed by alcohol, the entire apparatus may be weighed without exceeding the capacity of the microbalance. In either case, policing, with its technical difficulties, is avoided.

Results

Analyses were run on approximately 0.01 *N* sulfuric acid solution and 0.01 *M* potassium chloride solution, and several attempts were made to analyze for minute amounts of sodium according to the method of Barber and Kolthoff(*1*). The results of some typical analyses of sulfuric acid and potassium chloride are given in Table I.

Table I—Analyses of Sulfuric Acid and Potassium Chloride

Concentration of Sample	Amt. of Sample	Wt. of Precipitate	Wt. of Original Material Found in Sample	Error	Remarks
	Cc.	*Mg.*	*Mg.*	%	
			SULFURIC ACID[a]		
0.0101 *N*	5	5.95	2.5	+0.95	Weighed tubes on analytical balance
0.0101 *N*	5	5.90	2.48	+0.1	Weighed tubes on analytical balance
0.0101 *N*	2	2.375	0.998	+0.7	
0.0100 *N*	1	1.100	0.442	−0.53	
0.0098 *N*	2	2.282	0.9588	−0.24	Used acetone
0.0098 *N*	1	1.150	0.4832	+0.33	Used acetone
0.0098 *N*	1.5	1.720	0.7227	+0.2	Used acetone
			POTASSIUM CHLORIDE[b]		
0.0100 *M*	1	1.44	0.749	+0.4	
0.0100 *M*	2	2.835	1.474	−1.2	
0.0100 *M*	1	1.41	0.733	−1.7	
0.0100 *M*	1	1.435	0.746	0	

[a] Precipitate, barium sulfate. [b] Precipitate, silver chloride.

The weighings were carried out in all cases, except the two noted on Table I, on a microbalance with a sensitivity of about 0.005 mg. The weights of the precipitates amounted in most cases to a little over 1 mg. It is seen immediately that a considerable part of the errors observed fell within the error of the balance. The filter tubes average about 2 grams in weight, and in all cases they were weighed with use of a glass tare of practically the same weight. Consequently, it is believed that the limiting factors in the use of this apparatus are, first, the sensitivity of the balance used, and second, small variations due to occlusion of precipitant, solubility of precipitate, and so forth, and are not to any appreciable extent due to inherent difficulties with the apparatus itself.

As stated above, various attempts to use this apparatus for analysis of sodium according to the method of Barber and Kolthoff were made. Although their method is essentially micro in its original form, it is not necessary to use a microbalance. When samples containing about 2 mg. of sodium were used exactly as they describe, excellent results were obtained, but on reducing the sample to between 0.05 and 0.06 mg. of sodium, using this apparatus and the microbalance, erratic and usually low results were obtained. Deviations of from 5 to 25 per cent were common, and no way of adapting the method was found.

The advantages of this apparatus over that of Pregl are several. This one can be used for any method in which he uses the glass filter (*3*, p. 136) as in halogen and phosphate determinations. It can also be used in place of the micro-Neubauer crucible in the determination of sulfate. An accuracy as great as Pregl reports for sulfate determinations is not claimed for this method, for his method of ignition and rewashing is not easily adapted to this apparatus. However, it is felt that an accuracy of ±0.1 per cent is rarely necessary on such small samples as are here used, and the saving in time and labor is very considerable over his method. In the determination of sulfur by combustion as described by Pregl (*3*, p. 152), difficulty due to a large volume might be encountered. Since it is only necessary to weight the filter tube *B*, it is possible to make the reaction chamber *A* as large as desired so that this difficulty is readily overcome. No loss of precipitated barium sulfate through the filter is necessary if it is properly coagulated by heating and the asbestos pad is made from fine enough fiber. This apparatus is decidedly less costly than the micro-Neubauer crucibles and much more simply manipulated. A much smaller amount of glass is weighed than with Pregl's glass filter tubes, and here again the manipulation is simpler. Likewise, the speed of filtration is decidedly greater, since there are several holes in the platinum disk, each one of about the same diameter as the single hole in the glass filter tube. The amount of asbestos is also smaller.

Many other uses in gravimetric analysis may suggest themselves. It should, for example, be entirely feasible to carry out gravimetric calcium analyses by this procedure, if the suggestion of Willard and Boldyreff (*4*) of igniting the oxalate to carbonate at 450° C. is followed. In biological work, it is frequently desirable to use gravimetric methods for small amounts of organic materials, and here the determination might be simplified by use of this apparatus.

Literature Cited

(1) Barber, H. H., and Kolthoff, I. M., *J. Am. Chem. Soc.*, **50**, 1625 (1928).
(2) Kirk, P. L., and Schmidt, C. L. A., *J. Biol. Chem.*, **83**, 311 (1929).
(3) Pregl, F., "Quantitative Organische Mikroanalyse," 3rd ed., Springer, 1930.
(4) Willard, H. H., and Boldyreff, A. W., *J. Am. Chem. Soc.*, **52**, 1888 (1920).

Determination of Smoking Point of Fats[1]

John M. McCoy

Meat Inspection Laboratory, Bureau of Animal Industry, Washington, D. C.

THE smoking point of a fat is the lowest temperature at which sufficient decomposition takes place to produce visible smoke. As is well known, all fats decompose when heated to sufficiently high temperatures, with the formation of a variety of volatile substances, the most characteristic and familiar of which is acrolein. When observed under appropriate conditions, these volatile decomposition products appear as visible smoke.

The significance of the smoking point has been recognized for some time. Blunt and Feeney (*1*) studied the factors affecting the smoking point, its bearing on the utilization of fats, and described a method for its determination. Although this method is suitable for the comparison of different fats, at the same time it does not take into account all of the factors which may cause variation in the smoking point observed, and on that account is not satisfactory for use by various observers working in different laboratories and at different times. A more exactly standardized method is therefore required.

In the work of this laboratory, it has been found desirable to determine the smoking point on a number of samples of fats submitted for examination. As soon as the work was undertaken, the need of a standard method became evident. Accordingly, the method described was developed. The apparatus used, pictured in Figure 1, is simple, the time required for making determinations is short, and the degree of accuracy is sufficient for the purpose.

The method consists in heating the fat under uniform conditions until smoke appears, and noting the temperature. In preliminary experiments it was found that the smoking point is affected by the rate of heating and conditions of observation. Possibly the area of the surface exposed to air is also a factor. In order to attain uniform results, it is necessary, therefore, to heat a definite quantity of fat in a container of standard size and dimensions and observe the smoke under standard conditions.

Electric heaters of the type commonly used for Kjeldahl digestions (Gilmer heaters) were selected for heating. A rheostat is connected in series with the heaters so that the rate of heating can be reduced as the anticipated smoking point is approached Two heaters are connected in series with the rheostat. The top of one heater is covered with an asbestos plate with a $2^1/_4$-inch (5.71-cm.) circular opening in the center, the other by a similar plate with a $^7/_8$-inch (2.22-cm.) opening.

Figure 1—View of Apparatus

The containers used are standard 100-cc. round-bottom flasks, 6 cm. in diameter with 6-cm. neck, and made of Pyrex glass.

To make the smoke more readily distinguishable, a black screen 11 × 14 inches (27.94 × 35.56 cm.) in size and made of dull black cardboard, such as is used to protect photographic paper from light, is placed directly behind the heaters.

[1] Received June 22, 1931.

Natural light was found unsuitable on account of its variability. It was found necessary, therefore, to standardize the lighting. Accordingly, the apparatus is set up in a relatively dark place and dependence placed on artificial light. A lamp designed for microscope illumination, equipped with a 100-watt bulb and daylight glass, is used for illumination. The daylight glass renders the smoke more readily visible than it would be by uncorrected artificial light. The smoke point should, therefore, be observed by corrected artificial light.

The apparatus must be set up in a place which is protected from drafts, as even a moderate current of air affects accuracy.

Procedure

Melt the fat, allow moisture and suspended matter to settle out, and filter. Pour 50 cc. of the melted fat into the flask. Set the flask on the heater which has the large opening in the cover plate. Suspend the thermometer from overhead so that the bulb is immersed in the fat, leaving the flask unstoppered. Heat the fat to between 110° and 115° C. Then remove the flask to the other heater, placing it in such a position that its open mouth is illuminated by a horizontal beam of light from the lamp and viewed against the black screen. The lamp should be placed as near the heater as practicable to secure maximum intensity of illumination. Adjust the rate of heating with the rheostat so that the temperature rises at the rate of approximately 2° C. per minute. Take the temperature at which the first wisp of smoke is seen rising from the top of the flask as the smoking point. The first wisp of smoke should be followed by a plainly visible and continuous stream. Remove the thermometer when smoke is first observed. Smoke should then be seen issuing from the mouth of the flask. If not, replace the thermometer and continue heating until smoke again appears and continues after the thermometer is removed. In such case, the temperature at which the second appearance of smoke is noted is taken as the actual smoking point.

The method described has been in use for more than a year and has given satisfactory results. After proficiency has been acquired, duplicate determinations made on separate portions of the same fat should agree within 1° or 2° C. Closer agreement might be attained by slowing the rate of heating in the final stage.

Literature Cited

(1) Blunt, K., and Feeney, C., *J. Home Econ.*, **7**, 535 (1915).

Solubility of Water in Aviation Gasolines[1,2]

Elizabeth W. Aldrich

Bureau of Standards, Washington, D. C.

A method is described for the measurement of the solubility of water in liquid petroleum products, which is applicable to the determination of traces of water in many organic liquids. Sodium-potassium alloy free from oxide is added to a weighed sample of the water-saturated liquid after the removal of dissolved gases. The hydrogen evolved is collected and measured. Data are given on the solubility of water in five aviation gasolines at three temperatures.

The amount of water which collects in traps and carburetors is of considerable interest to the operators of automobiles and airplanes. Even after precautions have been taken to remove all suspended water from gasolines, there remain very small amounts of dissolved water. A decrease in temperature will cause the separation of some of the dissolved water which, if collected in the fuel feed system over a sufficient period of time, may stop the flow of gasoline to the engine. The flow may also be interrupted by the accumulation of partially hydrated aluminum oxide formed by prolonged contact of water with aluminum fittings. In winter weather, water in the fuel feed system may freeze and damage traps and carburetors.

When water dissolves in a gasoline, the total vapor pressure of the gasoline increases by an amount dependent upon the degree of saturation. When saturated, the partial pressure of water vapor is not measurably different from the vapor pressure of pure water at the existing temperature. This abnormally large increase in the vapor pressure caused by the presence of small amounts of water indicates the necessity for complete removal of dissolved water or the saturation with water at all temperatures when making accurate vapor-pressure measurements on gasolines. Accordingly, the amount of water required for the saturation of gasolines at various temperatures is of interest. The results of the present study indicate that the solubility at room temperature is about 1 part of water in 10,000 parts of gasoline, from which it may be concluded that all commercial gasolines are normally saturated with water when used in internal-combustion engines.

Although the solubility of water in gasolines is of interest in connection with a number of problems, very little data on the subject could be found in the literature. Apparently none of the methods previously used for the measurement of the amount of water in solution in gasoline are above criticism. Accordingly, an investigation was made of the method based on treatment of the gasoline with an alloy of sodium and potassium and determination of the volume of hydrogen evolved. Data for a number of aviation gasolines were obtained.

Choice of Method

Previous Methods—A number of methods (*1*) have been described for the measurement of the water in petroleum products. Of these only two seem to be sufficiently precise for the quantitative determination of the water dissolved in gasolines.

The first of these was used by Groschuff (*4*), who measured the solubility of water in kerosene, benzene, and paraffin oil. The temperatures were determined at which turbidity appeared and disappeared when known amounts of the liquid and water were cooled and heated in sealed tubes. In this phase change method it is difficult to determine when all the water is dissolved, since the water tends to stick to the side of the tube. It is also difficult to prevent undercooling.

The second method is that developed by Clifford (*3*). Air dried over calcium chloride was bubbled through water-saturated gasoline, and the air and vapors obtained were led through weighed calcium chloride tubes. Gasoline vapors

[1] Received March 17, 1931. Presented before the Division of Petroleum Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

were then removed by passing dry air through the calcium chloride tubes for several hours. However, the vapor pressure of water above calcium chloride is approximately 0.2 mm. of mercury, so that a loss of water vapor would be expected by this method since, during the period while water is being absorbed in the weighed tube, the dried air is diluted with gasoline vapor and the partial pressure of water vapor in it is reduced below 0.2 mm.

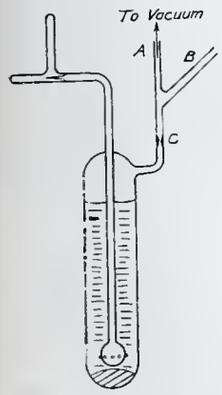


Figure 1—Shaking Tube for Saturating Gasoline with Water

Checks were obtained on samples containing known amounts of water, and it is possible that the loss of water vapor was compensated for by incomplete removal of gasoline vapors from the calcium chloride tube. However, the generality of this compensation for gasolines containing different amounts of water is doubtful.

Present Method—The method adopted is a refinement of the method (*1*) in which the hydrogen liberated by sodium is used as a measure of the water present.

The procedure may be divided into five steps:

(1) The saturation of the sample of gasoline with water by shaking for a predetermined time at a constant temperature.
(2) The transfer of a known weight of water-saturated gasoline to a suitable container filled with dry air.
(3) The removal from the gasoline of those constituents which exert more than a very small pressure at liquid air temperatures.
(4) The introduction of sodium-potassium alloy with resultant evolution of hydrogen.
(5) The separation of the hydrogen from the gasoline frozen in liquid air and its measurement in a buret at a determined temperature and pressure.

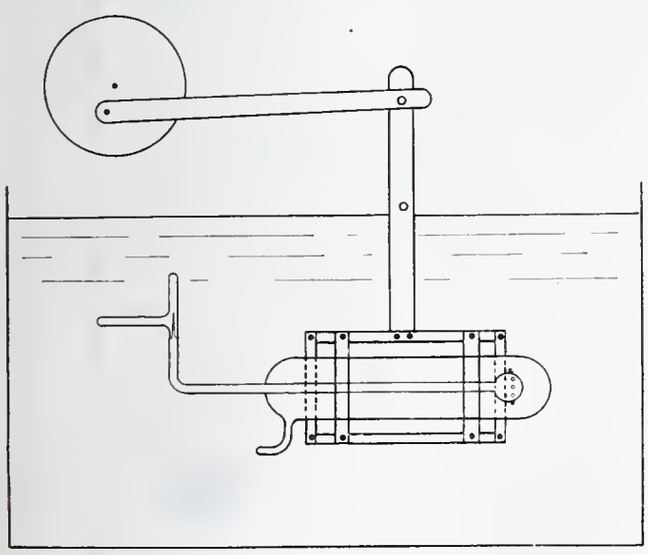


Figure 2—Schematic Diagram of Shaking Mechanism

The advantages of the method which led to selecting it for the present work are:

(*a*) A very small amount of water will yield an easily measurable volume of hydrogen.
(*b*) It involves only the reasonable assumption that the sole hydrogen-producing reaction is that between water and the alloy. In principle, it is otherwise free from serious sources of error.

The disadvantages of the present method are:

(*a*) It is complicated and time-consuming.
(*b*) The removal of all dissolved gases before the hydrogen is evolved and measured requires special equipment and technic.
(*c*) Any oxide in the alloy will introduce errors.

In view of these facts, it appears that, although capable of yielding the results required, the method is not especially adapted as a general one for determining the amount of water in gasoline, and that work on simpler methods would probably be more profitable than further development of this one.

Detailed Description of Apparatus and Procedure

Saturation of Gasolines with Water—The shaking tube used for the saturation of the gasolines with water is shown in Figure 1. It is a Pyrex glass bulb of about 100 ml. capacity, fitted with an inner tube. At the lower end of the inner tube is a small bulb with eight or ten holes about 1 mm. in diameter. The passage of the gasoline through these holes minimizes the carrying over, during transfer to a second bulb, of any of the undissolved water which settles to the bottom of

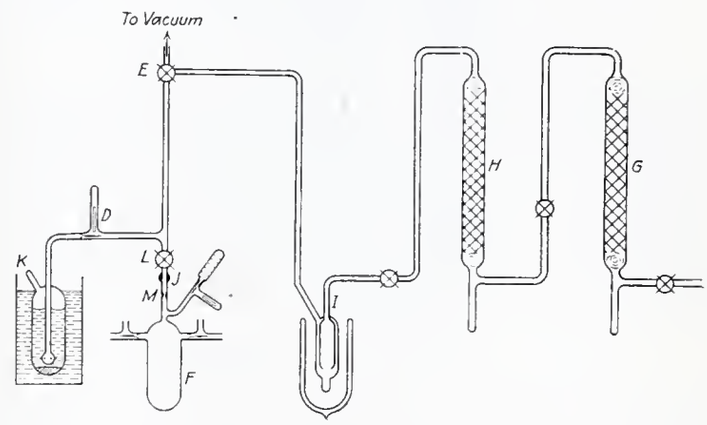


Figure 3—Apparatus for Sampling Water-Saturated Gasoline

the shaking tube. To the upper end of the tube is fused a magnetic seal which furnishes a means of transferring a sample of the gasoline to the analytical apparatus. The use of the magnetic seal, which consists of a thin glass tip sealed within a glass tube having a side arm, will be described later.

The shaking tube is sealed to the vacuum system through the side arm *A*. The vacuum is produced by a rotary pump which is capable of evacuating to approximately 0.001 mm. of mercury. Further evacuation to better than 0.0001 mm. may be effected by means of a mercury diffusion pump. Pressures are read on a McLeod gage connected to the vacuum line.

Approximately 60 ml. of gasoline and 1 ml. of water are introduced into the shaking tube through the side arm *B*. The tube is immersed in liquid air, and when the gasoline is frozen, the arm *B* is sealed off. The space above the gasoline is pumped to a pressure of approximately 0.01 mm., and the bulb sealed from the line at *C*. Evacuation at this time is necessary to avoid the pressures which would otherwise be developed on shaking the tube at higher temperatures and which would introduce difficulties in transferring the sample to the analytical apparatus.

The tube containing the gasoline and water is placed in a holder and shaken for 4 hours in a thermostated bath held at the desired temperature within 0.1° C. A schematic diagram of the shaking mechanism is shown in Figure 2.

In order to determine the time of shaking required to ensure saturation of the gasolines, a number of preliminary experiments were made in which samples were shaken with water for various lengths of time. The data on samples of fuel 19 shaken at 30° C. for 1, 2, and 4 hours are given in Table I. These data show that 1 hour is sufficient to saturate the gasoline under these conditions. In the solubility measurements, the gasolines were shaken for 4 hours, since a somewhat longer time might be required for saturation under some conditions.

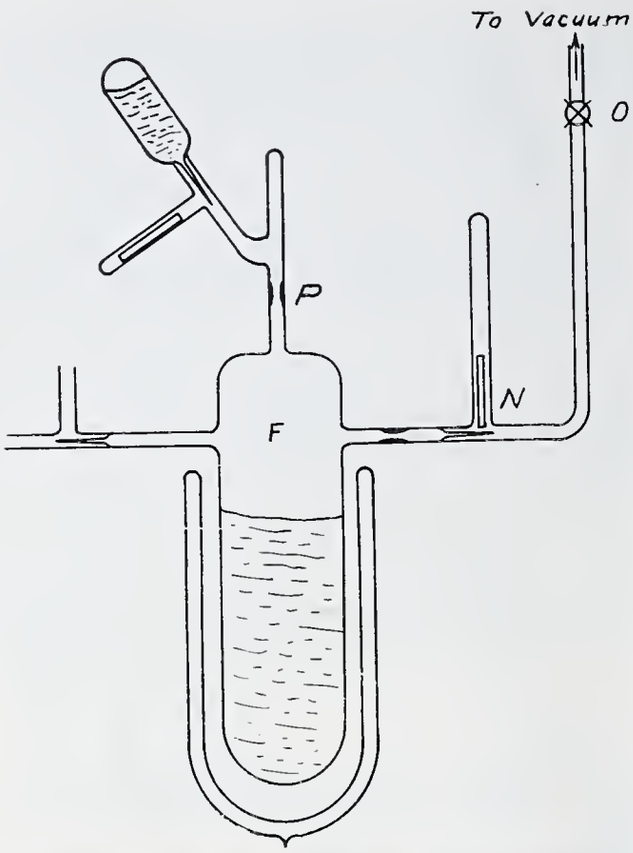


Figure 4—Apparatus for Removal of Dissolved Gases

Transfer of Water-Saturated Gasoline to Analytical Apparatus—After 4 hours of shaking, the tube is rapidly transferred to a second thermostated bath held at the temperature of saturation and regulated to 0.1° C. The ends of the two glass tubes leading from the magnetic seal are broken, a piece of iron inserted above the tip in the vertical tube at *D* (Figure 3) and this tube sealed. The other arm at *D* is connected by glass tubing to the bulb *F* and to the two-way stopcock *E*, which can be opened either to the vacuum or to the air. Three side arms equipped with magnetic seals are fused to the bulb *F*, one of them containing a sample of sodium-potassium alloy. This bulb is weighed before connecting it to the line by means of de Khotinsky cement at *J*.

Table I—Weight Per Cent of Water in Fuel 19 after Shaking for Various Lengths of Time

Shaking for 1 Hour	Shaking for 2 Hours	Shaking for 4 Hours
Wt. %	*Wt. %*	*Wt. %*
0.0065	0.0066	0.0074
....	0.0046	0.0057
....	0.0061	0.0056
....	....	0.0051
....	....	0.0056
Av. 0.0065	0.0058	0.0059

The stopcock *E* is opened to the vacuum, and the bulb *F* and the line leading to the tip at *D* are heated and pumped to remove all moisture. Ordinarily this did not take more than half an hour. Removal of moisture at this time is necessary, since the amounts of water which would ordinarily be contained in the air in bulb *F* would be approximately equal to the amount dissolved in the sample of gasoline.

Dry air is then admitted by opening the stopcock *E* to the air line. The air is dried by passage through the tube *G*, containing calcium chloride, the tube *H*, containing phosphorus pentoxide, and the bulb *I* which is immersed in liquid air. The amount of air admitted depends on the vapor pressure of the gasoline at the temperature of the bath.

When the vapor pressure is less than 760 mm., the pressure within the bulb *F* is adjusted until it is slightly less than atmospheric. The tube at *K* is broken so that the gasoline in the shaking tube is under atmospheric pressure. The tip at *D* is then broken by drawing the piece of iron to the top of the vertical tube by means of a magnet and letting it fall. Sufficient pressure is applied at *K* to force a sample of gasoline over into *F*.

In those cases where the vapor pressure of the gasoline is greater than atmospheric, dry air under pressure is forced into *F* and the magnetic seal is then broken. The gasoline is drawn over from the shaking tube by gradually reducing the pressure in *F* until it is slightly less than the vapor pressure of the gasoline. When 30 or 40 ml. of gasoline have been collected in *F*, the stopcock *L* is closed. The shaking tube is removed from the remainder of the system by breaking the horizontal glass tube connecting it to the bulb *F*. The broken end of the line is then sealed off. The gasoline in *F* is frozen in liquid air, the space above it evacuated, and the bulb *F* sealed from the line at *M*. *F* is weighed, together with the glass tube from *M* to *J* which is taken from the line by breaking the de Khotinsky seal *J*. The increase in the weight of the bulb *F* gives the weight of the gasoline sample.

Removal of Dissolved Gases—Those constituents of the gasoline which exert a considerable pressure at liquid air temperatures must be removed, or these gases would be measured together with the hydrogen in the final step of the procedure in which hydrogen is pumped from the frozen gasoline.

The bulb *F* is connected to the vacuum line as shown in Figure 4, through the magnetic seal *N*. A piece of iron is placed in the tube above the tip at *N*, and this tube sealed. The space between *N* and the stopcock *O* is evacuated, and after the gasoline in *F* has been cooled to liquid air temperatures, the tip at *N* is broken, using a magnet. The air and gases above the gasoline are pumped off, and with the stopcock *O* closed, the gasoline is warmed up to room temperature. The gasoline is again frozen and pumped. This procedure is repeated until the pressure above the gasoline after freezing but before pumping is less than 0.002 mm. The bulb is then sealed from the line.

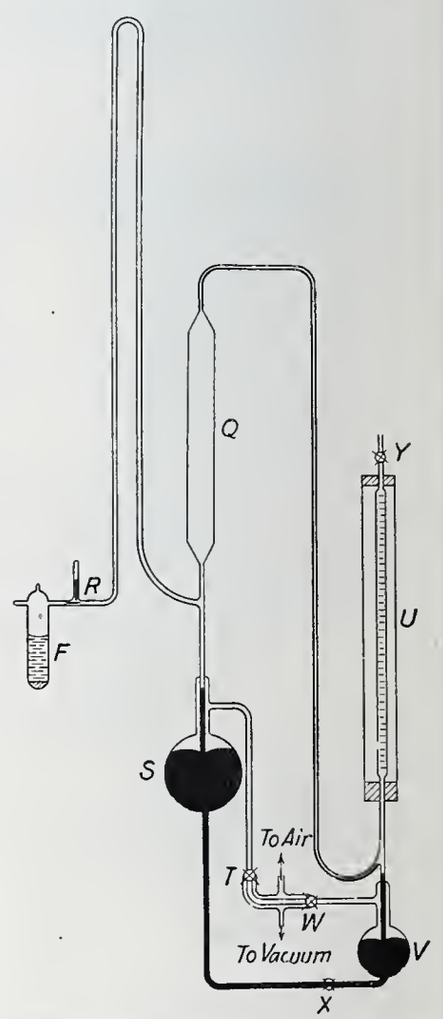


Figure 5—Apparatus for Separation and Measurement of Hydrogen

Introduction of Sodium-Potassium Alloy—With the gasoline frozen in liquid air, the magnetic seal holding the sodium-potassium alloy is broken and the alloy allowed to run into the bulb. The tube is then sealed off at *P*. The gasoline is warmed up to room temperature or slightly above, and at intervals is shaken vigorously. The decomposition of the water by the alloy with resultant evolution of hydrogen is

usually complete within 4 or 5 hours. The use of sodium-potassium alloy involves the reasonable assumption that no gas is evolved by reaction of the alloys with the hydrocarbons constituting the gasoline.

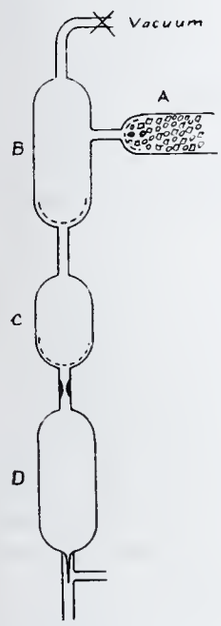


Figure 6—Apparatus for Preparation of Sodium-Potassium Alloy

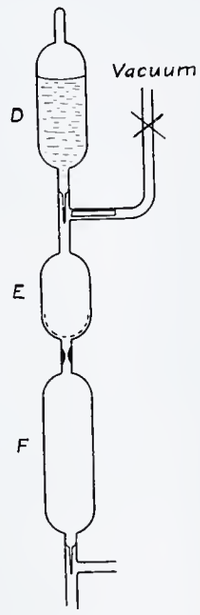


Figure 7—Apparatus for Purification of Sodium-Potassium Alloy

Separation and Measurement of Hydrogen—The apparatus used for removing the hydrogen from the gasoline and for measuring its volume is shown in Figure 5. The bulb F containing the gasoline and hydrogen is connected through the magnetic seal R to the long inverted U-tube leading to the mercury displacement pump Q, of approximately 200 ml. capacity. The pump is connected at the bottom to the mercury reservoir S which can be opened either to pressure or vacuum through the two-way stopcock T. A capillary tube from the top of the pump joins it to the buret U, graduated in 0.2 ml. The buret is enclosed in a water jacket and is connected at the bottom to the mercury reservoir V. This reservoir can also be opened either to vacuum or to pressure through the stopcock W. The stopcock X affords a means of transferring mercury from one reservoir to the other by proper adjustment of the pressures. The height of the U-tube above the surface of the mercury in S must be greater than 760 mm. to avoid forcing mercury over into the sample when pressure is applied in S.

The buret and pump are evacuated by opening to the vacuum through the stopcock Y. During evacuation, the pressure in S is adjusted so that the mercury does not rise to the joint with the inverted U-tube. The pressure in V is also adjusted so that the mercury does not close the capillary tubing. When the system is evacuated, the stopcock Y is closed and the mercury in V run up into the buret just above the joint with the capillary tube. The gasoline is frozen in liquid air and the magnetic seal at R broken. Air is admitted through T and the hydrogen in Q is displaced into the buret by the mercury from S. As soon as the mercury has run over into the buret, T is opened to the vacuum and the mercury in Q is drawn back into S. Time is allowed for the diffusion of hydrogen from F into Q, and this in turn is displaced into the buret. This process is repeated until all of the hydrogen above the frozen gasoline is collected in U. The efficiency of the pump depends upon the ratio of the volume of the bulb Q to the volume of the space between the top of the gasoline surface and the point at which the connecting tube joins Q. In the present case this ratio was approximately 7 to 1.

When all of the hydrogen above the gasoline has been displaced into the buret, the mercury in S is run up close to the top of Q. The liquid air surrounding the gasoline is removed and the gasoline allowed to warm up to room temperature. Care is taken that the pressure of the vapors does not become so high that gas is bubbled through the mercury. This process liberates additional hydrogen. The gasoline is again frozen and the hydrogen pumped off as before. These operations are continued until no further hydrogen is collected in the buret.

The hydrogen is allowed to stand until it reaches the temperature of the water jacket. The stopcock W is opened to the atmosphere, and the difference between the barometric pressure and the height from the mercury surface in V to the mercury surface in U gives the pressure of the hydrogen. From the volume of hydrogen under these conditions of temperature and pressure, the weight of water which was dissolved in the known weight of gasoline is computed.

Preparation of Sodium-Potassium Alloy

Sodium-potassium alloy, rather than either sodium or potassium alone, is used to liberate hydrogen from the water dissolved in the gasoline samples, because the alloy, when made up of approximately equal amounts of sodium and potassium, is liquid at room temperatures and can therefore be more easily introduced into the samples. The use of alloy instead of either sodium or potassium alone is also preferable because the liquid alloy maintains a fresh active surface.

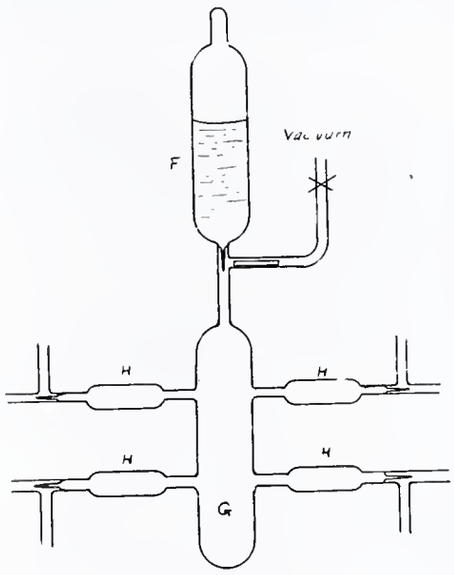


Figure 8—Apparatus for Subdivision of Sodium-Potassium Alloy

Complete evolution of the hydrogen can be accomplished only if the alloy is entirely free from oxides, since the oxides react with water without the liberation of hydrogen. It is necessary, therefore, to remove all oxide from the alloy and to store it in small samples in containers of a design suitable for introducing it into the gasoline without allowing it to come in contact with air.

Diagrams of the apparatus used in the preparation of the alloy are shown in Figures 6, 7, and 8. The apparatus shown in Figure 6 consists of the three Pyrex bulbs B, C, and D, and the side arm A. The whole system is sealed to the vacuum line. The bulbs are connected by heavy-walled glass tubing or by constrictions, and just above each constriction is placed a fine-mesh copper screen which hinders the passage of oxide while allowing the alloy to pass through. The lower end of bulb D is closed with a magnetic seal. Small pieces of sodium and potassium in approximately equal amounts are

placed in the side arm A, and the open end is then sealed off. The bulbs are opened to the vacuum, but complete evacuation at this point is not practicable because the removal of all the kerosene in which the sodium and potassium were stored requires an extremely long time. While the system is being pumped, the side arm is heated to melt the sodium and potassium. When the pressure is reduced to approximately 0.01 mm., the tube leading to the vacuum line is sealed off and the apparatus tipped until the alloy runs from the side arm into the bulbs, finally collecting in bulb D. This bulb is then sealed off at the constriction.

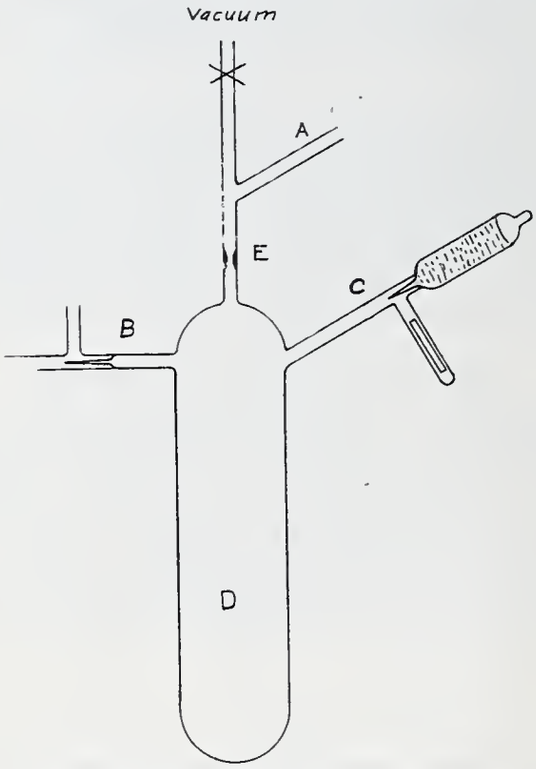


Figure 9—Apparatus for Drying Gasolines

The alloy contained in D is further purified using the apparatus shown in Figure 7. This consists of the two bulbs E and F, similar to those used in the first step of the preparation of the alloy. The bulb D is sealed to these two bulbs, a piece of iron introduced into the side arm, and this arm sealed to the vacuum line. The bulbs E and F are then evacuated to 0.0001 mm., and the magnetic seal broken. The alloy runs through the screen in E and is collected in F. The space above the alloy is again evacuated. The operation described above is repeated, after which the alloy is usually free from oxide, though occasionally it is necessary to filter again.

The final step is the subdivision of the large amount of alloy in F into individual samples which can be transferred to the gasolines without coming in contact with air. Figure 8 shows the apparatus used. The bulb G usually has as many as twelve side arms, H, each of which is closed by a magnetic seal. The bulb F is sealed to G and a piece of iron placed in the side arm which is then fused to the vacuum line. The bulb G and the arms H are evacuated to 0.0001 mm., and the magnetic seal broken. The alloy is collected in G, which is then sealed from the line. The bulb G is tilted until each side arm is separately filled with about 2 ml. of alloy and sealed off. These individual samples are then ready for use in the experiments previously described.

Test of Method

The accuracy of the method used for determining the water dissolved in gasolines was tested by several experiments in which known amounts of water were added to previously dried gasolines. A comparison could then be made between the amount of water added and the amount computed from the hydrogen evolved.

The apparatus used for drying the gasolines is shown in Figure 9. The bulb D, with the side arm magnetic seal B and the side arm C containing a sample of sodium-potassium alloy, was fused to the vacuum line. Gasoline was introduced through A and frozen in liquid air in the bulb D. The tube A was then sealed off and the space above the gasoline evacuated. The bulb D was next sealed from the line at E, and with the gasoline still frozen, the tip in C was broken, allowing the alloy to run into the gasoline, after which C was sealed from the bulb. The gasoline was allowed to warm up and stand with frequent shaking until no further hydrogen was evolved.

The next step in the procedure was the removal of the hydrogen and dissolved gases from the dry gasoline and the transfer of a sample into a second bulb. This was accomplished by means of the apparatus shown in Figure 10. The bulb D containing the gasoline was sealed to the vacuum line and to the bulb F as shown. The bulb F had three side arms, H, I, and J. The arm H contained a weighed amount of water; I, a sample of sodium potassium alloy; and J furnished a means of connecting the bulb to other apparatus without contact with air at a later step in the procedure. The bulb F was thoroughly evacuated and, with the gasoline frozen in liquid air, the tip at B was broken. The hydrogen and dissolved gases were then pumped off by a method similar to that previously described.

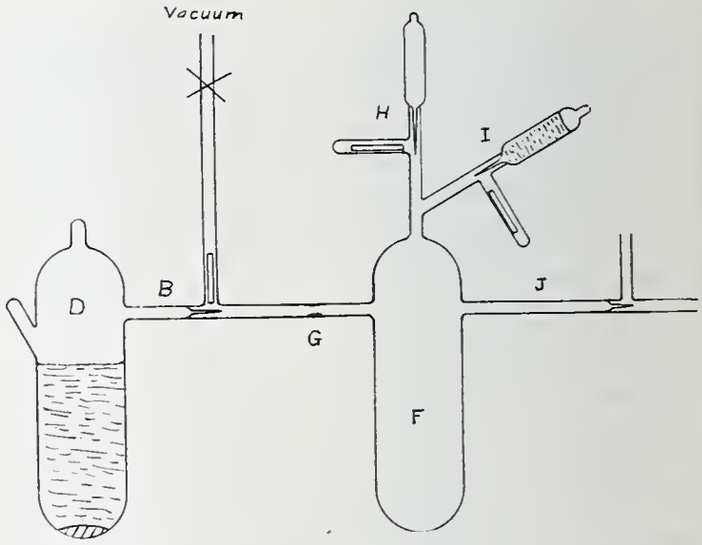


Figure 10—Apparatus for Addition of Water to Dry Gasolines

The dry, gas-free gasoline in D was distilled into the bulb F, which was then removed from the system by sealing at G, the tip at H was broken with the gasoline frozen, and the water condensed into F. The alloy was then allowed to run into the gasoline by breaking the tip at I, and the two arms H and I were sealed off from F. The alloy was shaken with the gasoline which was allowed to warm up. Finally the hydrogen evolved was removed from the gasoline by means of the mercury displacement pump and measured in a buret as described in the general method.

A comparison of the amounts of water added to 50 ml. of fuel 15 with the amounts computed from the hydrogen evolved is shown in Table II. Considering the difficulty of weighing out such small amounts of water, the agreement is good.

Table II—Comparison of Amounts of Water Added and Amount Found by Analysis

Water Added	Water Found
Gram	*Gram*
0.0025	0.0029
0.0019	0.0025
0.0024	0.0022

Experimental Data

The method described above was used to measure the solubility of water in five aviation gasolines at the temperatures 10°, 30°, and 50° C. A description of these gasolines is given in Table III and their specification data in Table IV.

Table III—Description of Gasolines

Fuel	Source
10	Oklahoma natural gasoline
12	West Virginia natural gasoline
13	California crude
15	Midcontinent crude
19	Oklahoma natural gasoline

Table IV—Specification Data on Gasolines

Fuel	Temperature At 10%	Temperature At 50%	Temperature At 90%	Loss	Residue	60°/60° Specific Gravity
	° C.	° C.	° C.	%	%	
10	42	64	110	2.3	0.9	0.677
12	68	80	110	0.4	1.8	0.695
13	68	93	124	1.3	1.3	0.733
15	68	101	139	1.4	1.3	0.718
19	48	65	110	1.6	1.2	0.682

The data recorded for each measurement are the volume, temperature, and pressure of the hydrogen. From these data the weight of water in the known weight of gasoline is computed, and finally the weight of water in 100 grams of gasoline according to the equation

$$S = \frac{57.78 \times 10^{-3}}{W}\left[\frac{PV}{t + 273.1}\right]$$

In this equation, S is the solubility in weight per cent, P is the pressure of the hydrogen in millimeters of mercury, V is the volume of hydrogen in milliliters, t is the temperature of the hydrogen in °C., and W is the weight of the gasoline sample in grams.

The data recorded and the solubility values computed from them are given in Table V. The solubility is very small and is roughly of the same order of magnitude for the fuels investigated—namely, 0.01 per cent. Based on check determinations, the average deviation in solubility is 0.0006, so that the precision of the method may be taken as somewhat greater than 0.001.

Table V—Data on Solubility of Water in Gasolines

Fuel	Temp. of Saturation	Wt. of Sample	Hydrogen Vol.	Hydrogen Temp.	Hydrogen Pressure	Solubility
	° C.	Grams	Ml.	° C.	Mm.	Wt. %
10	10	24.04	6.61	31.2	246	0.0128
	30	29.59	8.67	26.0	283	0.0160
	50	21.17	7.87	28.2	271	0.0193
12	10	22.01	3.05	31.0	193	0.0051
	30	33.56	4.91	26.0	237.5	0.0067
	50	32.29	5.26	29.5	237	0.0074
13	10	24.66	3.99	29.0	212	0.0066
	10	18.98	3.81	34.2	201	0.0076
	30	32.82	4.99	27.0	236	0.0069
	50	37.84	8.15	32.0	270	0.0110
	50	20.27	5.44	28.7	215	0.0111
15	10	22.84	3.27	32.0	214	0.0058
	10	30.00	4.01	35.0	211	0.0053
	30	31.06	8.67	25.0	295	0.0158
	30	28.17	9.79	26.5	279	0.0187
	50	28.41	10.39	27.0	295	0.0208
19	10	22.35	2.61	31.5	163	0.0036
	30	32.05	3.93	26.0	214	0.0046
	30	29.35	3.91	28.2	216.5	0.0061
	30	25.87	3.81	28.0	217	0.0057
	30	22.25	3.28	26.1	196.5	0.0056
	30	29.25	4.22	25.3	205	0.0056
	30	30.08	3.49	28.0	207	0.0051
	30	20.14	3.23	26.0	211	0.0066
	30	28.54	5.76	26.5	262.5	0.0065
	30	27.50	5.81	24.2	239.5	0.0074
	50	31.05	4.59	27.2	220.5	0.0063

The solubilities are also shown graphically in Figure 11 as a function of the temperature. With the exception of fuel 15, the data do not suggest that they should be represented by anything except straight lines. In the case of fuel 15, the change of solubility with temperature is much greater than for the other gasolines. Since duplicate values at 10° C. were in good agreement, the data on this fuel should be given equal weight with those on the other fuels. This exception probably vitiates any general conclusions regarding the temperature coefficient of solubility, other than that the solubility increases with increasing temperature.

The apparent exception observed in connection with fuel 15 is not unexpected when the effect of chemical composition on water solubility is considered. Thus Groschuff and Clifford have found that the solubility of water in benzene is approximately five times that in gasoline, and that the temperature coefficient of solubility is much greater than that for gasoline. Similar differences might be anticipated between the different hydrocarbon series. While the composition of fuel 15 is not known, it might reasonably be expected that there would be differences in the temperature coefficient of water solubility between gasolines from widely differing crudes or of diverse composition.

Comparison with Previous Results

The only data found in the literature on the solubility of water in gasolines were obtained using the calcium chloride method. Clifford (*3*) measured the solubility of water at three temperatures in a gasoline of specific gravity 0.70 and his results are as follows:

Temperature	Solubility
° C.	Wt. %
25.0	0.0085; 0.0110
35.0	0.0161; 0.0121
37.5	0.0175; 0.0145

The Army Air Corps (*2*), using the same method, found that the solubility of water in a domestic aviation gasoline at 75° F. (23.9° C.) was 0.007 per cent by weight.

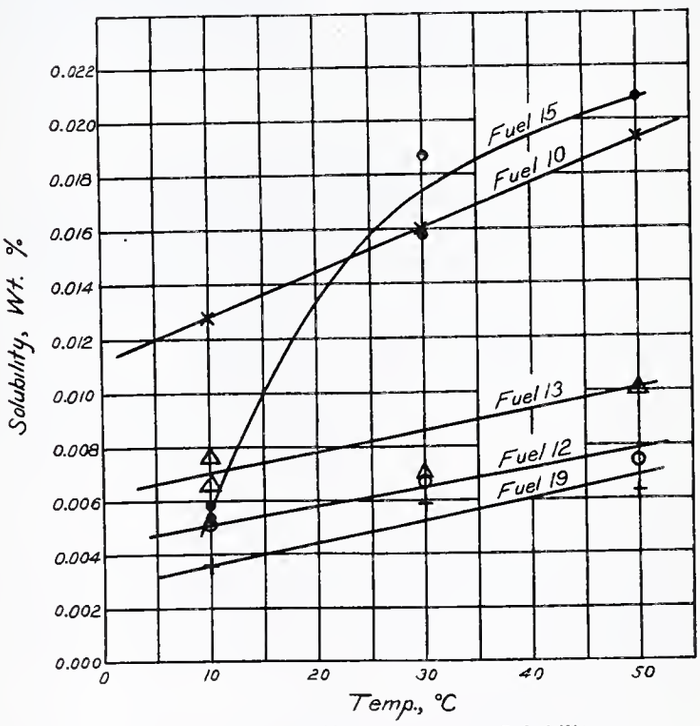


Figure 11—Effect of Temperature on Solubility

This same method was used by Uspenskii (*5*) to measure the solubility of water in four gasolines at two temperatures. The results obtained are as follows:

Gasoline	Solubility 10° C.	Solubility 22° C.
	Wt. %	Wt. %
Grozny "avis"	0.007	0.011
Grozny, grade I	0.006	0.008
Grozny, grade II	0.006	0.008
Baku, grade II	0.005	0.008

The values obtained by these investigators are of the same order of magnitude as those found in the present work.

and all of the results are in agreement that the solubility of water increases with increasing temperature. The only indication of the precision of the calcium chloride method is given by the duplicate determinations of Clifford, which show an average deviation from the mean values of 0.0016, as compared with 0.0006 by the sodium-potassium alloy method. However, too few data have been obtained by either method to justify too close a comparison of the relative precisions. Since the increased precision found was obtained by a very marked increase in the complications and time involved, additional work on simpler methods might be more profitable than further development of the method used in the present investigation.

Acknowledgment

This investigation was undertaken as part of a fundamental study of vapor lock in airplane fuel systems in coöperation with the Research Committee of the Society of Automotive Engineers, and was made possible by a contribution from the Naturaline Company of America.

Literature Cited

(1) Allen and Jacobs, Bur. Mines, *Tech. Paper* **25** (1912).
(2) Army Air Corps, *Air Service Information Circ.* **320** (1922).
(3) Clifford, J. Ind. Eng. Chem., **13**, 628 (1921).
(4) Groschuff, *Elektrochem.*, **17**, 348 (1911).
(5) Uspenskii, *Neftyanoe Khozyaistvo*, **17**, 713 (1929).

Determination of Small Quantities of Sulfur and Chlorine When Present in Turpentine[1]

W. C. Smith

Industrial-Farm Products Division, Bureau of Chemistry and Soils, Washington, D. C.

Small quantities of sulfur and chlorine in turpentine can be determined quantitatively by using the Kennedy sulfur lamp with A. S. T. M. Method D-90-26T. Sulfur was found in all samples of refined sulfate wood turpentine tested. Chlorine was found in only three out of ten samples tested. The sulfur content of well-refined sulfate wood turpentine is so small as to escape detection by the usual qualitative methods.

Within the past few years there has appeared on the naval-stores market of this country spirits of turpentine recovered during the manufacture of paper pulp from pine wood by the sulfate process. This class of turpentine is known both here and in Europe as sulfate wood turpentine.

Except as regards odor, sulfate wood turpentine can be made to meet the generally accepted specifications for gum spirits of turpentine or steam-distilled wood turpentine. The odor of refined sulfate wood turpentine, while mild and inoffensive, is characteristic. It can be readily distinguished from the odor of gum spirits or the usual steam-distilled wood turpentine, but may be confused with the odor of the turpentine obtained in the soda process of pulp making.

Crude sulfate wood turpentine is known to contain sulfur compounds. Although no reference to the sulfur content of refined sulfate wood turpentine was found, it was thought that this product might contain sufficient of these compounds to serve as another means of identifying this class of turpentine. Samples of authentic gum spirits of turpentine, of steam-distilled wood turpentine, of refined sulfate wood turpentine from each concern in this country known to produce this product, and in addition samples from several lots of imported sulfate wood turpentine, were used for the tests herein described.

The usual qualitative tests made on the turpentine itself did not show the presence of sulfur in any of the samples. The results obtained in tests with a sodium peroxide bomb were not satisfactory on account of the limitation of the size of the sample used. It was found that by a tedious process of oxidizing a 5- or 10-cc. portion of a sample with fuming nitric acid and precipitating any sulfuric acid formed as barium sulfate, the presence of sulfur compounds in the turpentine could be detected. The fuming nitric acid oxidation method, besides being dangerous because of the extremely violent reaction, does not give concordant results and therefore cannot be used quantitatively.

The American Society for Testing Materials has adopted a method, D-90-26T (*1*, *2*), for determining sulfur in naphthas and illuminating oils. This method consists, briefly, of burning the oil for a specified time in a weighed lamp made from a small Erlenmeyer flask. The gases of combustion are drawn by suction from the chimney through a known quantity of standard sodium carbonate solution. At the end of the specified time, the flame is extinguished and the lamp is again weighed. The quantity of oil used for the determination is found by the difference in the two weights of the lamp. A blank determination is made at the same time by burning alcohol in place of the oil. The excess of sodium carbonate is titrated with standard acid. From the difference in the quantity of sodium carbonate neutralized by the blank and the oil determination, the quantity of sulfur in the oil can be calculated.

In attempting to apply the lamp method of the American Society for Testing Materials for sulfur, it was found impossible to burn turpentine with a smokeless flame. This difficulty was overcome by diluting a volume of the sample with two volumes of absolute ethyl alcohol, but it was still necessary to watch the operation closely, and it required too much time to burn a sufficient quantity of turpentine to give satisfactory results. In place of the lamp mentioned above, the Kennedy sulfur lamp (*4*) with slight modification was found more suitable for the purpose. In fact, turpentine was burned with a smokeless, luminous flame without the addition of alcohol. For the best operation of the lamp in burning turpentine, it was found necessary to insert in the tube leading from the fuel regulator to the vaporization chamber a wick of long-fiber asbestos to insure even feeding, to reduce the inside diameter (mouth) of the burner to 2 mm., and to replace after a few runs the plug of glass wool in the vaporization chamber.

With the Kennedy lamp in connection with Method D-90-26T, samples of sulfate wood turpentine and also authentic samples of gum spirits and steam-distilled wood turpentine were tested for sulfur. Excellent checks were obtained on duplicate tests. Whenever this method indicated the presence of sulfur, a confirmatory test was made by transferring

[1] Received April 25, 1931.

the absorption solution, after neutralization, to a beaker, adding bromine water, boiling, and precipitating with barium chloride. In the case of samples 11, 12, and 13 it was noted that the weights of barium sulfate obtained by this check corresponded to smaller quantities of sulfur than was indicated by the titrations.

It was known that calcium and sodium hypochlorite have been used in refining crude sulfate wood turpentine (*3*). This suggested that the difference between the total acidity obtained by the lamp combustion and the quantity of sulfur recovered as barium sulfate might be due to chlorine.

The three samples on which the difference was found were retested with the lamp, and the absorption solutions were acidified with nitric acid and treated with silver nitrate solution. In each case silver chloride was precipitated, which on weighing indicated sufficient chlorine to account for the difference between total acidity by titration and sulfuric acid by precipitation of the barium sulfate. Chlorine was not found in the other samples tested. The results obtained with the various samples are listed in Table I.

Table I—Results of Tests of Various Samples for Sulfur with Kennedy Lamp

Sample	Kind of Turpentine	Sulfur	Chlorine
		%	%
1	Gum spirits	None	None
2	Gum spirits	None	None
3	Steam-distilled wood	None	None
4	Steam-distilled wood	None	None
5	Steam-distilled wood (soda process)	None	None
6	Sulfate wood (Sweden)	0.016	None
7	Sulfate wood (Sweden)	0.013	None
8	Sulfate wood (Sweden)	0.015	None
9	Sulfate wood (U. S. A.)	0.015	None
10	Sulfate wood (U. S. A.)	0.013	None
11	Sulfate wood (U. S. A.)	0.013	0.24
12	Sulfate wood (U. S. A.)	0.011	0.28
13	Sulfate wood (U. S. A.)	0.012	0.16
14	Sulfate wood (U. S. A.)	0.016	None
15	Sulfate wood (Canada)	0.017	None

Although the absorption method of determining sulfur in volatile fuels has been well tried out and has been in general use for some time, it was thought best to test the accuracy of this method for use with turpentine.

A small quantity of ethyl mercaptan was added to gum spirits of turpentine previously found to contain no sulfur, and three 5-cc. portions of this solution were tested for sulfur, with the following average result:

Sulfur Added	Sulfur Found
%	%
0.054	0.052

To test further the accuracy of this method for chlorine determination, solutions of purified pinene hydrochloride in both turpentine and ethyl alcohol were burned and the gases absorbed. Almost theoretical yields of chlorine were obtained. It was found that practically all the chlorine passed into the absorber in the form of hydrochloric acid. The results obtained when turpentine containing mono- and dichlorobenzene were burned in the Kennedy lamp indicated that the chlorine in these compounds is also converted quantitatively into hydrochloric acid on burning.

On the other hand, bromine compounds of turpentine and benzene on burning in the Kennedy lamp, were found to yield bromine and bromic acid in about equal proportions.

That the sulfur compounds in refined sulfate wood turpentine are concentrated in the lower boiling portions is indicated by the following results on fractions of sample 9:

Fraction	Sulfur
	%
Distilling below 156° C.	0.030
Distilling 156–158° C.	0.008
Distilling 160–162° C.	0.004

The first 5 per cent of distillate of sample 15 obtained from distilling 200 cc. through an 8-inch (20.32-cm.) Hempel column was found to contain 0.072 per cent sulfur. A similar concentration of chlorine compounds was found in the lower boiling fractions of certain of the samples of sulfate wood turpentine. This suggests that, where the presence of sulfur and/or chlorine in turpentine is in doubt, the results obtained by submitting the low boiling fraction obtained on distillation to the lamp combustion test can be relied on to determine definitely whether these two elements are present in the turpentine.

Literature Cited

(1) American Society for Testing Materials, "Tentative Standards," 1927.
(2) Bur. Mines, *Tech. Paper* **323B** (1927).
(3) Jobson, C. A., U. S. Patent 1,493,454 (May 6, 1924).
(4) Kennedy, Ind. Eng. Chem., **20**, 201 (1928).

Some Factors Influencing Soap Tests for Hardness[1]

R. H. Kean and H. Gustafson

International Filter Company, Chicago, Ill.

THE soap test method of determining hardness in water, while lacking the accuracy of an analytical procedure, is nevertheless capable of giving a very fair approximation of the true value in the hands of an experienced operator, and where it is used upon a single water for the purpose of measuring variations in hardness, the results have a considerably greater degree of reliability. There are certain factors, however, which may affect its accuracy even under these favorable conditions and, therefore, certain precautions must be observed to avoid the possibility of error. The necessity for these precautions arises from the fact that the test actually measures the soap-consuming power of the water rather than its hardness, and any condition of the water tending to promote or inhibit the formation of lather, or tending to decompose or precipitate the soap, may thus introduce errors into the determination.

[1] Received April 8, 1931. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind. March 30 to April 3, 1931.

This paper presents the results of an investigation of the errors introduced by certain conditions frequently encountered in zeolite water-softening practice—namely, by variation in the temperature of the water, by the presence of free carbon dioxide, and by the presence of certain salts of sodium. The experimental work was conducted with Boutron and Boudet soap solution, the standardization of which specifies that 40 cc. of water containing 225 p. p. m. of hardness as calcium carbonate shall require 2.4 cc. of soap to produce a lather. This is equivalent to 72 drops of soap, the droppers being calibrated to deliver 30 drops to the cubic centimeter. Thus 5 drops are equivalent to each 15 p. p. m. of hardness, or about $5^1/_2$ drops for each grain per gallon, making no allowance for the soap required to produce a lather with water containing no hardness.

The temperature of the water has a very considerable influence on the soap test, there being an apparent increase in hardness with decreasing temperature. This is shown on Figure 1, which is a correction chart for this effect. The range

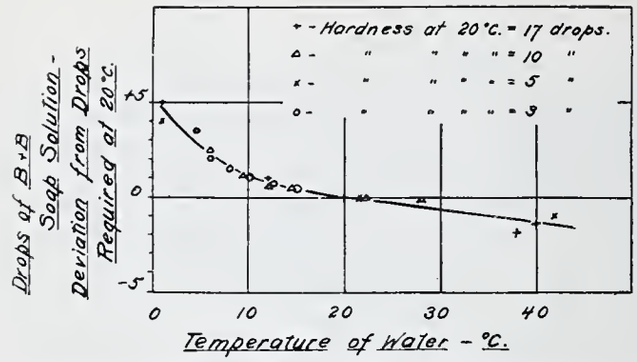


Figure 1—Correction Chart for Effect of Temperature on B. and B. Soap Test

below 10° C. is the only part of the curve having significance for work in the field, but here the correction assumes real importance. For instance, in Chicago, where the winter temperature of the water is 1.5° to 2.0° C., the error amounts to 4 drops of soap. Since softener runs are often terminated when the effluent requires 5 drops, this test would indicate that the softener was incapable of delivering water softer than 1 grain per gallon, whereas in reality the water would be of "zero" hardness, requiring 1, or at most, 2 drops of soap. The effect of temperature is independent of the true hardness of the water up to 3 or 4 grains per gallon, the increase in soap requirement being identical for a "2-drop" water and a "15-drop" water.

Like low temperature, free carbon dioxide is a very disturbing factor. In the field its influence appears to be exceedingly erratic, owing in part to its fugacity, in part to the poor end point that it causes, and in part to the fact that its effect varies with the alkalinity of the water, the hardness, and other factors. Thus a simple correction chart for its influence cannot be constructed. However, its effect can be stated in more general terms, and a typical example is illustrated by Figure 2. For instance, the increase in soap required for a

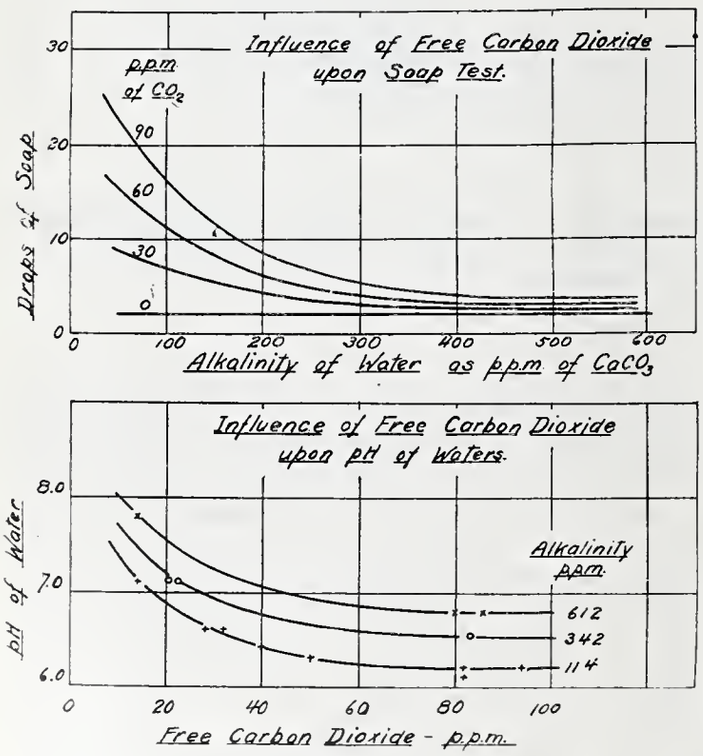


Figure 2

given water is approximately proportional to its carbon dioxide content, as is shown by the relative vertical distances between the line for the soap requirement of a water free of carbon dioxide, and the lines for 30, 60, and 90 p. p. m. of carbon dioxide Also, it has been found that a given content of carbon dioxide will cause a slightly greater increase in the soap requirement of a very soft water, say a "2-drop" water, than in the requirement of a harder water of 10 or 15 drops. Further, it may be seen from the chart that the influence of carbon dioxide decreases very markedly with increasing alkalinity of the water. This is owing to the repression of the hydrogen-ion concentration by the buffer action of the bicarbonate.

The lower chart on Figure 2 illustrates the relationship between hydrogen-ion concentration, alkalinity, and carbon dioxide content. It shows how a given carbon dioxide concentration produces a greater depression of the pH in waters of low alkalinity. Furthermore, a comparison of the two charts demonstrates that the depression of the pH and increase in soap requirement go hand in hand—that is, the lower the pH, the greater the soap requirement. This is the significant point, for it indicates that the effect is a function of hydrogen-ion concentration rather than of the carbon dioxide itself. It is substantiated by the fact that a similar increase in soap requirement is obtained with distilled water, free of carbon dioxide, to which minute quantities of mineral acid have been added. In such waters the increase in soap requirement is directly proportional to the quantity of acid added. The action is apparently a decomposition of the soap with liberation of fatty acid. The end point with mineral acid is very sharp, a copious lather being produced immediately when neutralization of the acid is complete. With carbon dioxide, however, as might be expected, the progressive shift of the equilibrium of the slightly ionized acids with successive additions of soap produces a poor lather and an uncertain end point.

The difficulty caused by the presence of carbon dioxide and mineral acid may be completely removed by adding to the soap solution sufficient sodium hydroxide to neutralize the acidity of the water, which reëstablishes very satisfactorily the proportionality between true hardness and drops of soap up to 3 or 4 grains per gallon. This expedient is very convenient for zeolite work where the waters tested lie within this hardness range, but the use of such alkaline soap for general field work is not recommended, because with larger amounts of soap solution the caustic concentration may become sufficient to effect some softening of magnesium waters and waters containing carbonate hardness.

It has been indicated on Figure 2 that increased alkalinity of the water is without effect on the soap test. This was ascertained by adding different amounts of sodium bicarbonate to a water of known hardness. Sodium chloride and sodium sulfate likewise have no effect up to concentrations of 2500 p. p. m. (150 grains per gallon). The only action to be expected from these neutral salts would be a salting-out of the soap but, within the limits of concentration encountered in water treatment, this does not occur.

Transparent Cellulose Covers for Nessler Comparison Tubes

To eliminate errors due to removal of stoppers on permanent standards when readings are made, transparent cellulose (cellophane) has been used as a cover over the opening of the Nessler tube. This cover can be held in place by means of a rubber band or by sealing it to the tube with label varnish. The color can be conveniently read through the cellophane cap. Dust and dirt cannot enter the solution, and there is no evaporation.

These cellophane caps can be used wherever color comparisons are performed with Nessler tubes.

E. Zimbon

Chicago Department of Health
Chicago, Ill.
May 7, 1931

Method for Determination of Small Quantities of Paraform in Various Mixtures[1]

Woltor Weinberger

1453 Walton Ave., New York, N. Y.

A method for determining paraform in certain typical mixtures is discussed, the experimental results obtained in seeking the method given, and the method described in detail.

The percentage error of a determination as carried out by this method is only 1 per cent. Romjin's method is found to be more reliable and accurate for the determination of formaldehyde in very dilute solutions than any other of the well-known methods.

THIS method may also be applied to the determination of formaldehyde in various mixtures, or to the determination in such mixtures of any easily decomposed compound or polymer of formaldehyde.

Commercial paraform is commonly known as paraform, paraformaldehyde, and trioxymethylene. It is apparently a mixture, of varying composition, of polymers of formaldehyde, each having the general formula $(HCHO)_n$. Since the name "trioxymethylene" has been specifically applied to a definite compound, $(HCHO)_3$, its use in describing such a mixture of polymers is misleading. Paraform is more accurately described as polyoxymethylene, or, as the author has done, following the suggestion of Austin M. Patterson, as polymerized formaldehyde. All quantitative results referring to paraform will be expressed in this paper in terms of formaldehyde, with the legend "formaldehyde in polymerized form."

Commercial paraformaldehyde is a product which is being widely used today as an antiseptic and disinfectant. It is generally met with as a white powder having an odor of formaldehyde. It is insoluble in ether and alcohol, sparingly soluble in cold water, and soluble in solutions of the fixed alkalies, with decomposition. When heated it is partly converted into formaldehyde, partly sublimed unchanged.

This compound is rarely used by itself as an antiseptic or disinfectant, but is most often mixed with talc and alkaline earths to make a dusting powder or an insecticide. Because of its increasing use, it was deemed advisable to find a rapid, reliable, and accurate method for its determination in such typical mixtures as paraform and talc, clays, earths, oxides of certain metals, borates, stearates, etc.

Method for Determination of Formaldehyde

The available methods of determining formaldehyde have been tried, and Romjin's method (*1, 2, 3*) adopted as the only one giving reliable results in solutions as dilute as the distillates. In mixtures of the type discussed, there seems to be no known method, and no method suggests itself, for determining paraform as such. This being so, two very obvious questions present themselves: (1) how to free the paraform from the large bulk of matter present (talc, etc.) and from any other foreign material which may interfere with the determination; and (2) having freed the paraform from interfering substances, how to determine its amount.

In freeing the paraform from the large bulk of matter, it must be remembered that we are dealing with a polymer of formaldehyde, which under ordinary conditions is prone to depolymerization, so that some formaldehyde must always be present. Therefore, all considerations which attach to the determination of small amounts of formaldehyde will also apply here. For instance, we cannot attempt to dissolve out the polymer with some suitable solvent, filter, evaporate, and weigh. Such a method is clearly unsuitable, even if the inert ingredients present would permit such a separation.

Again, paraform cannot be measured as such. Its constant depolymerization, even if very slight, would prevent this. The only possible method seems to be to transform the paraform into formaldehyde, to determine the formaldehyde, and to calculate the equivalent amount of paraform in accordance with the equation $(HCHO)_n = n(HCHO)$.

Paraform is broken down into formaldehyde by heat or steam, especially in the presence of dilute acids. Formaldehyde, as is well known, distils with water or with steam.

These considerations suggest, as an answer to the first question, some sort of distillation. But for quantitative results, under what conditions must we distil, and how great a volume must be distilled over? Then, these questions being answered, how shall we determine the formaldehyde in the distillates, which will necessarily be very dilute solutions?

The total available methods for determining formaldehyde have been tried in solutions of known formaldehyde content. the strengths of the solutions so used being comparable to those of the distillates.

The method of oxidizing formaldehyde to formic acid in accordance with the following equation

$$HCHO + H_2O + I_2 = 2HI + HCOOH$$

and titrating the excess iodine was found to be very unreliable for the determination of formaldehyde in these dilute solutions. The more usual peroxide–sodium hydroxide method was also found to be unreliable at such dilutions. Further experimental data showed that the results obtained by the bisulfite method and by the ammonia method could not be trusted where there was so much water and so little formaldehyde.

The method finally accepted as being reliable, and adopted, was the one depending on the fact that formaldehyde forms an additive product with cyanides, and that the cyanide so used does not react with silver salts.

A known weight of potassium cyanide is added to the formaldehyde solution. A definite volume of standard silver nitrate is then added. The silver cyanide formed is filtered off and the excess silver is determined in accordance with the following equations:

$$\begin{aligned} KCN + AgNO_3 &= AgCN + KNO_3 \\ KCN + HCHO &= KCNHCHO \\ AgNO_3 + KCNHCHO &= KCNHCHO + AgNO_3 \text{ (excess)} \quad (1) \end{aligned}$$

Experiments

A sample of paraform containing 97 per cent formaldehyde in polymerized form, when assayed in accordance with the method in the U. S. Pharmacopeia, 10th ed., page 277, was obtained.

Typical dusting powder mixtures (talc, alkaline earths, stearates, clay, borates, etc.) containing definite and known amounts of this paraform were prepared.

[1] Received September 8, 1930.

After trials of a number of types of distillation, the use of steam distillation was decided upon as the type which could be used with the utmost simplicity, neatness, and economy of time. When the ordinary distillation was attempted, the foaming was so uncontrollable as to require constant watching.

Typical experiments and some of the experimental results obtained are as follows:

(1) Twenty grams of a freshly prepared mixture, accurately weighed, were transferred to an 800-ml. distilling flask; 25 ml. of water plus 10 ml. of dilute sulfuric acid were added. The contents of the flask were then steam-distilled so that about 110 drops distilled over each minute, the volume in the flask being kept nearly constant. Various fractions of the distillate were collected, by definite volumes, in volumetric flasks. The formaldehyde in each fraction was determined in accordance with the cyanide method as sketched above, and given in detail after the conclusion. Qualitative tests for the presence of formaldehyde in each fraction were also made. For this purpose Schiff's reagent was used.

In place of listing each distillation separately, the results of a typical set of distillations is arranged in Table I. All distillations were run on freshly prepared samples.

Table I—Typical Set of Distillations

(Charge contains 0.0210 gram of formaldehyde in polymerized form)

	Formaldehyde Found in Distillate						Color Test with Schiff's Reagent
	2	3	4	5	6	Av.	
	%	%	%	%	%	%	
1st 50 ml.	48	49	50	47	48	48	Deep
2nd 50 ml.	24.3	25	24	26	25	25	Deep
3rd 50 ml.	12.8	13	12	14	13	13	Moderate
4th 50 ml.	6.7	7	6	6	7	7	Less
5th 50 ml.	4.3	4	3	3	4	4	Weak
6th 50 ml.	2.4	2	3	3	4	3	Perceptible
7th 50 ml.	0.5	..	..	..	..	0	Traces
8th 50 ml.	..	..	..	..	..	..	No color
Total	99.0	100	98	99	101		
Error	−1	0	−2	−1	+1	1	

(2) This work was repeated with several different mixtures and identical results were obtained. It must be remembered, of course, that the volume of liquid in the distilling flask and the rate of distillation were both kept very much the same for each distillation.

(3) Charges were varied so that it was necessary to distil amounts of formaldehyde ranging from 0.02 gram to 0.20 gram. In all cases similar results were obtained for each set of distillations in that the formaldehyde was practically completely carried over in 300 ml.

(4) Formaldehyde was added to the contents of the flask and distilled. One hundred per cent recovery was obtained, but determinations were made only within the range indicated in paragraph 3 above.

From a study and consideration of the foregoing results the following conclusions must be drawn: (1) Within the range studied, practically all of the formaldehyde present is in the first 300 ml. distilled over. (2) All but 5 to 10 per cent of the formaldehyde present is in the first 200 ml. distilled over. Therefore, for most purposes, and since the formaldehyde content of many commercial products is so small, it is sufficient to distil over only 200 ml. (3) The error of 1 per cent is probably an error inherent in the manipulations.

Method for Determination of Paraform

This method, or the operative details of it, is based on the results of the trial distillations and the conclusions drawn therefrom. It has been used for the determination of paraform in many different mixtures and has been found reliable and accurate.

In performing this distillation, certain theoretical considerations endemic to every steam distillation must be remembered. If the same percentage of formaldehyde is to be found in the same volume of distillate, the volume of liquid in the distilling flask and the rate of distillation as indicated here must be adhered to. It should also be kept in mind that the distillation was studied within a certain limited range.

Transfer 20 grams of the sample to an 800-ml. Kjeldahl flask.
Add 25 ml. of water and 10 ml. of dilute sulfuric acid.
Add paraffin to prevent foaming.

Steam-distil rapidly (about 110 drops per minute, keeping the volume in the distilling flask fairly constant), catching the first 300 ml., or 200 ml. if extreme accuracy is not desired, in a volumetric flask.

Into each of two 50-ml. volumetric flasks run, accurately, 9 ml. of 0.1 *N* silver nitrate. Add 6 drops of concentrated nitric acid.

To one of the flasks add an excess of potassium cyanide solution. A 0.1 *N* solution is easiest. Make up to the mark with water, shake, and filter. Pipet 25 ml. of the filtrate into a flask, add 5 ml. of ferric alum indicator, and titrate the excess silver nitrate with standard thiocyanate solution. This serves as a control.

Pipet 25 ml. of the distillate into a small beaker. Add the same amount of cyanide solution that was added to the control, and stir well. Transfer this solution to the other small volumetric flask, make up to the mark with water, shake, and filter. Pipet 25 ml. of this filtrate into a flask, add 5 ml. of ferric alum indicator, and titrate the excess of silver nitrate with the standard thiocyanate solution. The per cent of formaldehyde in polymerized form is as follows:

If 300 ml. have been distilled, (ml. KCNS for sample − ml. for control) × normality of KCNS × 3.6
If 200 ml. have been distilled, (ml. KCNS for sample − ml. for control) × normality of KCNS × 2.6

The charge taken and the aliquots used, as well as the amount of the cyanides and the strengths of the standard solutions, all depend, of course, on the amount of formaldehyde present.

Literature Cited

(1) Assocn. Official Agr. Chem., *J. Assocn. Official Agr. Chem.*, **8**, 67 (1925).
(2) Romjin, *Z. anal. Chem.*, **36**, 18 (1897).
(3) U. S. Dept. Agr., Bur. Chem., *Bull.* **132**, 49 (1910).

A Dish for Toxicity Tests[1]

A. S. Daniels

Southern Pacific Lines, Houston, Texas

IT HAS been pointed out that in testing the toxic properties of certain wood preservatives, the Petri dish is not satisfactory as it may permit the volatilization of some of the substance under test (*1*). Schmitz (*2*) has recommended placing the inoculated Petri dishes under small bell jars set on glass plates. Bateman and Henningsen (*1*) suggest glass-stoppered Erlenmeyer flasks in place of Petri dishes. Both of these methods have serious disadvantages, particularly when incubator space is limited.

The writer has found that the use of Stender dishes offers distinct advantages over any of the methods suggested. Cultures are plated and inoculated in Petri dishes in the usual way. A sterile 100-mm. Stender dish is then inverted on the table. The bottom is raised a few inches and the prepared Petri dish slid on to the Stender dish cover. The cover of the Petri dish is removed, the ground groove in the Stender dish cover is filled with melted hard vaseline, and the Stender dish gently lowered and fitted back in to the vaseline-filled groove of the cover.

Cultures so prepared can be stacked up to the capacity of the incubator, they are readily available for observation, and they effectually prevent the volatilization of any appreciable portion of the substance under test.

Literature Cited

(1) Bateman and Henningsen, *Proc. Am. Wood-Preservers' Assocn.*, **19**, 136 (1923).
(2) Schmitz, Ind. Eng. Chem., Anal. Ed., **1**, 76 (1929).

[1] Received May 29, 1931.

Sludge Ripeness Studies[1,2]

E. L. Pearson and A. M. Buswell

Illinois State Water Survey, Urbana, Ill.

In a study of the factors influencing the drying qualities of digested sludge, various well-known tests denoting the degree of digestion were applied to the sludges in question. Lack of correlation between some of the tests prompted this study of the older tests and a search for a new one which might be more usable. Since the way in which the tests are conducted has considerable influence on the results obtained, the methods used in this experiment will be briefly outlined.

Volatile Acids—A 200-cc. sample was acidified with 2 cc. of concentrated sulfuric acid and distilled until 100 cc. had come over; the distillate was titrated with 0.1 N sodium hydroxide and the alkali used calculated to acetic acid. According to the Duclaux distillation curves, this procedure gives approximately 35 per cent of the acetic acid present when distilled from distilled water solution, and a slightly higher percentage when distilled from a solution of the character of sewage sludge. In this experiment the results are reported as titrated and are, therefore, relative.

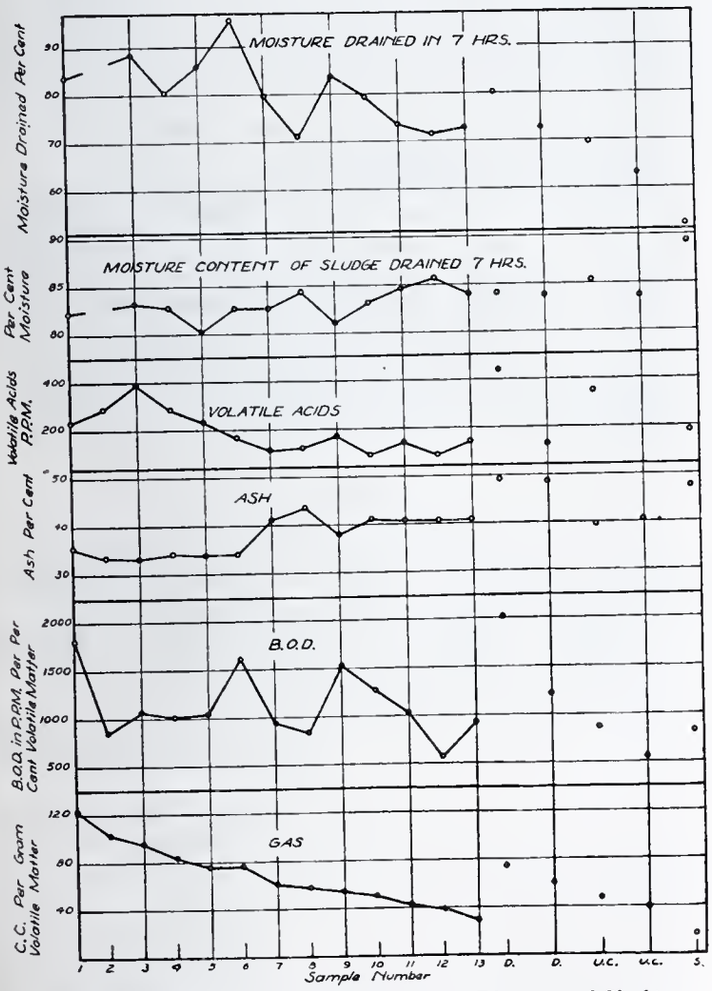


Figure 1—Results of Tests to Determine Ripeness of Sludge

Drainability—One liter of sludge was weighed and poured onto a $^3/_4$-inch (1.90-cm.) layer of standard Ottawa sand in a 28-mesh sieve. The amount of liquid drained in per cent of total present was plotted against time. The moisture remaining after 7 hours' draining was also determined. The weight of the sludge cake gave a check on the evaporation which was found to be negligible when the sieve is covered. In all cases, of the total moisture draining in 24 hours more than 90 per cent had drained in 7 hours. The drainability data given here are for a 7-hour period.

Ash—A 40- to 50-cc. sample was weighed in a platinum dish, evaporated on a steam bath, and dried for $1^1/_2$ hours at 105° C., weighed, and ignited in a muffle at 850° to 900° C. for 1 hour.

24-Hour Biochemical Oxygen Demand—A 10-cc. pipet (with tip broken off) graduated to tenths of a cubic centimeter was used to measure the sludge. Aerated distilled water with 500 p. p. m. of sodium bicarbonate was used as dilution water. A four- to fivefold increase in the dilution employed indicated a 40 to 70 per cent increase in B. O. D. The dilution was selected, therefore, which would result in the consumption of about half of the available oxygen. A duplicate determination using the same dilution checked reasonably well. The results are reported in parts per million per per cent volatile matter.

24-Hour Gas Production (*2*)—Five hundred cubic centimeters of sludge (or more, if gasification was slow) were placed in a bottle and connections made whereby the gas evolved could be collected over saturated salt solution and measured. The samples were incubated at 30° C. and rotated gently at the end of 5 or 6 hours, and again just before

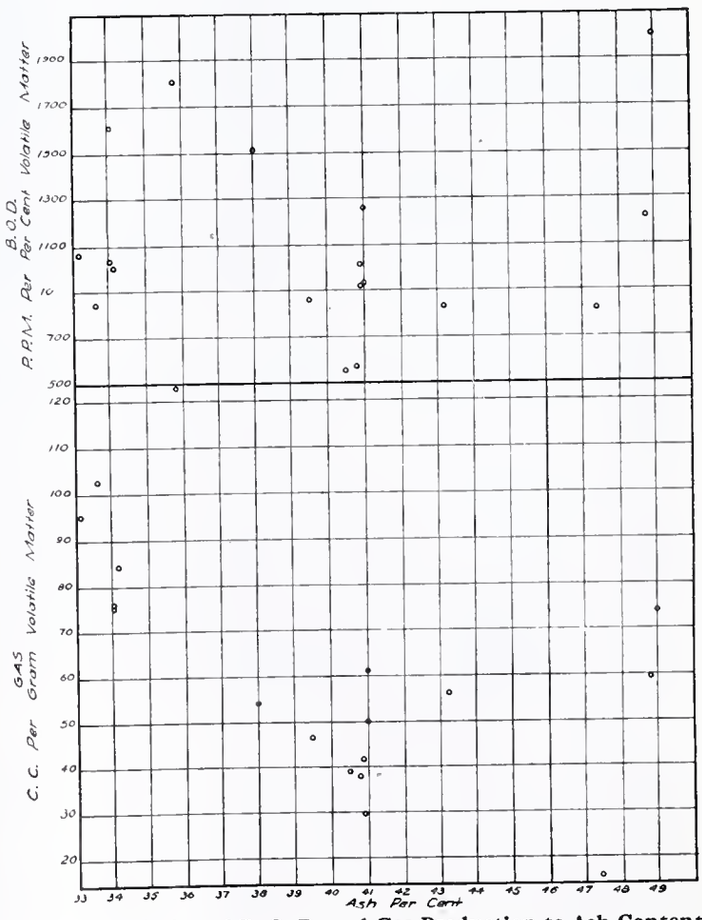


Figure 2—Relation of B. O. D. and Gas Production to Ash Content of Digested Sludge

[1] Received May 11, 1931. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] This work was carried out with the assistance of funds furnished by the Chemical Foundation.

measuring the gas. The gas produced was reported in cubic centimeters per gram of volatile matter in the sludge.

Before being connected to the gas collecting bottles, the samples were allowed to stand for 2 hours to avoid collecting the gas liberated by reason of a change in temperature or pressure.

Discussion—Figure 1 shows the results of these determinations as made on a series of sludge samples. The samples connected by lines were obtained from the experimental plant, those not connected were obtained from the Urbana-Champaign, Decatur, and Springfield sewage treatment plants. For purposes of comparison they are arranged in the order of their decreasing 24-hour gas production, considering the series as a whole. The results of the various tests show a general correlation. On individual samples, however, wide discrepancies are very evident. As indicated in Figure 2, the best agreement is between the ash and the 24-hour gas production determinations.

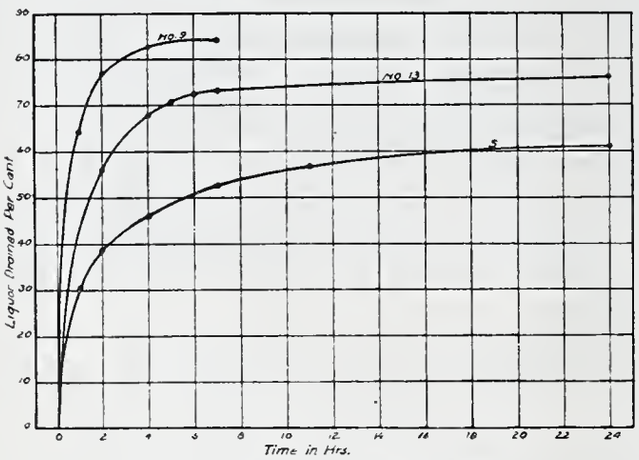


Figure 3—Sludge-Drainability Curves

Results of Tests

Drainability—Figure 3 shows typical drainability curves of a slow, a medium, and a rapid draining sludge. In general, the more thoroughly ripened the sludge, the poorer its draining qualities. The moisture which may be removed by draining, therefore, appears to be, within certain limits, in inverse relation to the degree of ripeness of the sludge. The percentage of the moisture removed by draining is lower and the amount of moisture retained by the drained sludge higher for a well-ripened sludge than for a partially ripened sludge. In view of this, the drainability is not strictly a function of the original solids content.

From these studies, the draining quality does not appear to be the important consideration in the drying of digested sludge. The ease with which the non-draining moisture is released and the character of the resulting cake appear to be of greater significance. A longer time is required to remove the smaller amount of remaining moisture in the better draining sludges, and a tough fibrous cake is produced instead of the porous granular material from well-ripened sludge. However, the better draining qualities, together with the fact that it is inoffensive and has been degasified, suggest the possibility that mechanical dewatering of this type of sludge might be more successful than has been the case with well-ripened sludge.

Volatile Acids—The volatile-acid content of a well-ripened sludge will be low, but a low volatile-acid content does not necessarily mean that the sludge is well ripened. The volatile-acid content is governed by the rate at which they are formed by the decomposition of more complex substances, and the rate at which they are decomposed to the gaseous end products. A rapidly gassing sludge may, therefore, be low in volatile acids. With batch feeding, following the course of the volatile-acid content in conjunction with the gas production would give an indication of the completion of digestion. With continuous feeding, however, the volatile acids have been shown to follow a trend opposite to that of gas evolution (*1*).

24-Hour Biochemical Oxygen Demand—The biochemical oxygen demand of this series of sludges shows, in general, a trend parallel to the other tests. It shows less correlation with the ash content, however, than does the 24-hour gas evolution.

From these studies it does not seem that a definite B. O. D. below which sludges are sufficiently ripe to draw can be set which will be applicable to sludges of all sources. Some sludges in this experiment having a B. O. D. below 1000 p. p. m. per per cent volatile matter, although inoffensive and non-putrescible, would hardly be considered ripe for drawing because of their unsatisfactory drying qualities and the character of the cake produced.

Ash Content—The ash content of the digested sludge is probably the most used ripeness test. Its significance is dependent on a knowledge of the ash of the fresh solids fed, and the results from one plant are not comparable to those of another plant whose fresh solids do not have a similar ash content, or where the ash determination is not carried out at the same temperature.

24-Hour Gas Production Test—As with the foregoing tests, the gas production of the series of sludges showed a trend similar to the results of the other tests, with wide variations, however, between the results on individual samples. At present it necessitates an ash determination, but it has advantages in its simplicity, in the large sample that may be used, and in the minimum apparatus and reagent requirements. If the gas evolution can be successfully correlated with the ripeness of a digested sludge, it should prove a useful test.

Conclusions

Within the limits of the degrees of ripeness shown by the series of sludges herein studied the following tentative conclusions may be drawn:

The draining quality of a digested sludge is roughly inversely related to its ripeness and to the ease with which the non-draining moisture is removed.

In the continuous feed process of sludge digestion, volatile acids are a better index of the course of digestion than of its degree of completion.

The ash and solids content of a digested sludge may be satisfactory locally as an indication of ripeness, but both are also dependent on other factors, and are, therefore, not of general applicability.

Most of the sludges from the experimental plant had a biochemical oxygen demand below 1500 p. p. m. (*2*) but were not considered sufficiently ripened to permit ready disposal.

Correlation of the rate of gas production under standard conditions with the ripeness of a digested sludge is being attempted.

Literature Cited

(1) Buswell and Pearson, "Further Studies on Rapid Stage Sludge Digestion."

(2) Rudolfs and Fischer, *Public Works*, **57**, 5, 171 (1926).

Expansion of Paint Industry in India—The paint industry of India is growing and each year is affording increasing competition to imported paint products, according to the Department of Commerce. There are now sixteen paint factories maintained by large British paint manufacturers. The other plants are relatively small and in most instances do not manufacture a complete line of paints. Varnishes and lacquers are not produced in India on a commercial scale at present.

Volumetric Barium Chromate Method for Sulfates[1]

J. R. Andrews

604 Chew St., Allentown, Pa.

Using the ferrous sulfate–permanganate titration for estimating the liberated chromate, the method of Hinman may be used in determining from 2 to 200 mg. of sulfate. From 0.5 to 2 mg. is determined by fortifying the water with 2 mg. of sulfate and deducting this from the amount recovered.

Hydrogen sulfide and other reducing matter present in the water are oxidized by potassium permanganate prior to the addition of the barium chromate reagent.

THE barium chromate method for the determination of sulfates has been adopted in some water laboratories with success. The results listed here indicate that this method may be applicable also to oil-well brines whose sulfate contents vary considerably with different samples. The method described by Hinman (*4*) in 1877 depends upon the fact that barium chromate is slightly more soluble in a neutral solution than barium sulfate; that when barium chromate is added to a soluble sulfate, the more insoluble barium sulfate is precipitated and a soluble chromate is formed. The soluble chromate is then determined in the filtrate by titration.

Schmidt (*3*) discussed the procedures recommended by Bruhns, Nachtigall and Raeder, and Koszegi. Schmidt, using a 0.2 *N* hydrochloric acid solution of barium chromate, recommends that the precipitations be carried out in the cold on the sulfate water as received, and that the final determination of soluble chromate be made by the iodometric method. Germuth (*1*) notes that the method of Wildenstein, using 0.02 *N* barium chloride followed by a slight excess of 0.02 *N* potassium chromate, is accurate and rapid.

The method recommended by Schmidt would not be satisfactory for oil-well waters, inasmuch as the precipitations are carried out on the water as received and many oil-well waters contain hydrogen sulfide, ferrous iron, and other reducing matter which would reduce the chromate and give low results. It appears that the method of Wildenstein would give very satisfactory results, since an excessive amount of chromate could be avoided regardless of the amount of sulfate present. Although an excessive amount of chromate is formed with high sulfate waters, Hinman's method appears to be simpler in that the standard solutions of barium chloride and potassium chromate are eliminated.

The following solutions are used in the suggested procedure:

Permanganate Reagent: Dissolve 0.5 gram of potassium permanganate in 100 ml. of water.

Barium Chromate Reagent: Dissolve 5 grams of barium chromate in a solution of 26 ml. of hydrochloric acid and 975 ml. of water. (10 ml. of this reagent should be used for precipitating each 15 mg. of SO_4^{--}, and a minimum of 10 ml. should be used for less than 15 mg. of SO_4^{--}.) The barium chromate should not contain sufficient soluble chromate or barium salts to give a titration difference greater than 0.05 ml. of standard permanganate in the following tests: Prepare two solutions, 1 and 2, each containing 2 mg. of chromium as sodium chromate in distilled water. Carry solution 1 through the procedure for the determination of sulfates as outlined in this paper, omitting the oxidation and reduction by the permanganate and peroxide reagents, and adding 30 ml. of the barium chromate reagent. To solution 2 add 2 drops of concentrated hydrochloric acid, 10 ml. of sodium acetate, and dilute to the same volume as occupied by solution 1 after the filtration. Add the same amount of sulfuric acid required by solution 1, and titrate the chromate. If the titrations on solutions 1 and 2 do not check within 0.05 ml. of standard permanganate, a soluble chromate or barium salt is indicated to be present in sufficient amount to cause an error in a sulfate determination. This deleterious salt is removed from the barium chromate by washing the powder with dilute acetic acid or by precipitating the barium chromate from dilute hydrochloric acid solution with ammonia water.

Sodium Acetate: Dissolve 250 grams of sodium acetate in 830 ml. of water.

Standard Ferrous Ammonium Sulfate: Dissolve 39 grams of the crystals in 950 ml. of water containing 50 ml. of sulfuric acid. This solution, about half again as strong as the standard potassium permanganate, is titrated against the permanganate each day a relation is required, and is kept in an amber-colored bottle in a cool place.

Standard Potassium Permanganate: Heat 1100 ml. of distilled water to boiling, add 1 ml. of permanganate reagent, and boil several minutes. Dissolve 1.975 grams of potassium permanganate in 1000 ml. of the cooled water prepared above. Standardize the solution against a sulfate water whose sulfate content is known, and adjust so that 1 ml. is equivalent to 2 mg. of SO_4^{--}. The sulfate waters used for standardization should be selected from those received for analysis in the regular course of the laboratory work, and are evaluated by the barium chloride–gravimetric method.

Procedure

Using methyl orange as indicator, neutralize 100 ml. of the boiling water, containing between 2 and 200 mg. of SO_4^{--}, in a 300-ml. conical flask, with concentrated hydrochloric acid, adding 2 or 3 drops in excess. Oxidize any reducing matter with permanganate reagent, avoiding an excess of more than 1 drop and continue to boil for a minute. Then destroy the permanganate color, or cause the precipitated manganese dioxide to dissolve, with a drop or two of 3 per cent hydrogen peroxide, and boil to expel the excess completely. Add 10 ml. of sodium acetate solution, and for each 15 mg. of SO_4^{--} present add 10 ml. of barium chromate reagent. In no case add less than 10 ml. of the barium chromate reagent. Finally, add 3 drops of concentrated ammonia water for each 10 ml. of barium chromate reagent and continue to boil 5 minutes.

Allow the solution to cool several minutes on the bench and then in tap water to 15° C. Occasional agitation while the solution is cooling assists the precipitation of that barium chromate which is soluble in the hot solution. Filter the supernatant liquid through a retentive paper into a 400-ml. beaker and agitate the precipitate remaining in the flask with 20 ml. of cold water. Wash the flask and filter with cold water, using 80 ml. altogether. Note that the precipitate is tinted yellow, indicating that an excess of barium chromate reagent was used.

For each 100 ml. of filtrate add 10 ml. of cold (1 to 1) sulfuric acid. Titrate with standard ferrous ammonium sulfate until the pale blue color of reduced chromium is evident, and add 2 ml. excess. After 1 or 2 minutes, back titrate with standard permanganate to the faint purple end point. The end point is very clearly seen against a white background when light from an electric lamp is used, but direct sunlight hides the end point. Look down through the solution from such an angle that a beam of light reflects from the bottom edge of the beaker.

Nachtigall and Raeder (*2*) recommend the use of hydrogen peroxide as an oxidizing agent, but permanganate appears to be better in that an excess can be avoided. An acid solution of peroxide reduces chromate so that the excess must be removed completely before the barium chromate reagent is added.

[1] Received May 5, 1931.

Rather than add a large excess of sodium acetate, the hydrochloric acid, added with the barium chromate reagent, is neutralized partially with ammonia water, leaving the solution slightly acid with acetic acid.

Table I—Analyses of Water with Sodium Sulfate Added

SO_4^{--} Present	SO_4^{--} Found (Av.)	Error (Max.)	
Mg.	*Mg.*	*Mg.*	%
0.00	0.85	+0.85	...
0.49	1.05	+0.60	122.0
0.97	1.31	+0.39	40.0
1.46	1.63	+0.26	18.0
1.95	2.03	+0.13	6.7
2.44	2.40	−0.09	3.7
2.92	2.90	−0.03	1.0
3.41	3.35	−0.15	4.4
3.89	3.73	−0.23	5.9
4.38	4.38	+0.05	1.1
4.86	4.69	−0.25	5.1
9.73	9.64	−0.09	0.9
12.18	11.95	−0.23	1.9
24.35	24.25	−0.10	0.4
48.71[a]	48.71	+0.39	0.8
73.1	73.6	+0.5	0.7
97.4	97.6	+0.2	0.2
121.8	121.5	−0.3	0.2
194.8	194.4	−0.4	0.2
0.00[b]	0.00	....	...
0.49[b]	0.54	+0.05	10.0
3.65[c]	3.55	−0.10	2.7
6.57[c]	6.63	+0.06	0.9

[a] Reference point at which solutions were standardized.
[b] 2 mg. of chromium as sodium chromate added.
[c] 170 mg. of magnesium chloride, 1700 mg. of sodium chloride, 220 mg. of calcium chloride added.

The results in the tables indicate that amounts of sulfates ranging from 2 mg. to 200 mg. may be determined with reasonable accuracy, and down to 0.5 mg. may be determined by adding 2 mg. of sulfate and deducting this from the amount recovered. Since 2 ml. of $N/29.2$ sulfuric acid contain 3.29 mg. of sulfate, this could be used as the source of sulfate.

When 2 mg. of chromium as sodium chromate were added to distilled water and the procedure for the determination of sulfates followed, omitting the oxidation and reduction by the permanganate and peroxide reagents and adding 30 ml. of barium chromate reagent, only 2 mg. of chromium were recovered. When distilled water alone was carried through the above procedure, a blank of 0.85 mg. of sulfate was obtained. These tests indicate that it is incorrect to deduct a blank from the titration figures, since the blank is obtained only on amounts of sulfate less than 2 mg. (Table I)—that is, when there are sufficient chromate ions in solution, the solubility of the barium chromate in weak acetic acid solution becomes negligible.

A study of the results in Table I indicates that the permanganate solution may be standardized against a solution containing 48.71 mg. of SO_4^{--} with a maximum error of 0.39 mg. This would give the standard permanganate an SO_4^{--} value with a maximum error of 0.8 per cent. However, by averaging several values at 48.71, the standard permanganate is made accurate within 0.2 per cent, as shown in the table where that accuracy was attained on 97.4, 121.8, and 194.8 mg. of SO_4^{--}. Since, on smaller amounts of SO_4^{--} than 24.35 mg., a small error in milligrams means a large percentage error in the evaluation of the solution, it is recommended that the permanganate be standardized against a minimum of 25 mg. of SO_4^{--}. The third column indicates the greatest error recorded in two or more determinations.

There are, of course, several other methods for the determination of chromates, such as the iodometric method and several electrometric methods. It appears that almost any of these methods would be suitable for this determination, although the permanganate end point in the ferrous sulfate–permanganate method is much more easily distinguished than is the starch end point in the iodometric method.

Literature Cited

(1) Germuth, *J. Am. Water Works Assocn.*, **19**, 607 (1928).
(2) Nachtigall and Raeder, *Arch. Hyg.*, **100**, 31 (1928).
(3) Schmidt, *Z. anal. Chem.*, **82**, 353 (1930).
(4) Treadwell-Hall, "Analytical Chemistry," Vol. II, p. 610, Wiley, 1928.

Comparison of Solubilities of Calcium and Strontium *p*-Bromobenzoates in Acetone-Water Mixtures[1]

John C. Bailar, Jr.

University of Illinois, Urbana, Ill.

THE similarity between the compounds of calcium and those of strontium is so great that difficulty is experienced in effecting a separation of the two metallic ions. According to Hillebrand and Lundell (*2*), "No really good methods for separating calcium, strontium, and barium from each other are known." The ratios of the solubilities of calcium and strontium salts in water are too small to offer satisfactory methods of separation. Fresenius (*1*) developed a method of separation based upon the difference in the solubilities of the nitrates in a mixture of equal amounts of absolute alcohol and absolute ether. Although the solubility ratio in this case is very large, Fresenius reported that the results for strontium were high, whereas those for calcium were correspondingly low. The method of Rawson (*3*) depends upon the fact that calcium nitrate is soluble in concentrated nitric acid, whereas strontium nitrate is not appreciably soluble. This method also gives high results for strontium. Another instance is reported here in which there is a rather large solubility ratio, and which, it is hoped, may ultimately be developed into a good method of separation.

Water dissolves the *p*-bromobenzoates of calcium and strontium to the extent of 2 per cent at room temperature. The addition of acetone to the water solution decreases the solubilities of both salts, that of strontium *p*-bromobenzoate much more than that of the calcium salt. Under optimum conditions, the ratio of the solubilities in a water-acetone mixture is about 45 to 1.

Practically all of the metal *p*-bromobenzoates are insoluble in pure acetone, but acetone which contains a little water dissolves many of them. The alkali and ammonium *p*-bromobenzoates are soluble to the extent of 1 per cent in acetone which contains 6 per cent water. The reagent used in experiments in this laboratory was a saturated solution of ammonium *p*-bromobenzoate in 94 per cent acetone. This reagent was mixed with water solutions of calcium and strontium nitrates. Fifteen cubic centimeters of acetone were then added for each cubic centimeter of the water solution that was used, bringing the acetone concentration again to 94 per cent. Under these conditions, a solution of strontium nitrate containing 1 mg. of the salt per cubic centimeter gives a distinct crystalline precipitate, and a solution of calcium nitrate fifty times as concentrated remains perfectly clear.

[1] Received April 29, 1931.

Experiments of this sort gave rise to the hope that this was a method of separating calcium and strontium quantitatively. Unfortunately, however, the solubility of strontium *p*-bromobenzoate is remarkably increased by the presence of other metallic ions, including the calcium ion. A solution containing equal amounts of calcium and strontium nitrates gives a very slight precipitate, even when the concentration of the strontium salt is 10 or 15 mg. per cubic centimeter. If the concentration of calcium nitrate is increased to three or four times that of the strontium nitrate, precipitation is entirely prevented. All efforts to avoid this difficulty have been unsuccessful.

In the hope of effecting a separation of calcium and strontium, comparisons have been made of the solubilities of several other halo-benzoates of these two metals. In no other case, however, was there any great difference in solubility, either in water or in water-acetone mixtures. Qualitative tests have shown that if a chlorine, bromine, or iodine atom is in the ortho position to the carbonyl group, the salts are many times more soluble in 94 per cent acetone than if the halogen atom is in the para position; the few meta-substituted salts studied show an intermediate solubility. In any case, the solubility decreases markedly with increasing atomic weight of the halogen. Table I gives the solubilities of the para-substituted salts in 94 per cent acetone at room temperature. (The ortho- and meta-salts were not studied quantitatively.) It will be seen that all of the *p*-iodobenzoates are quite insoluble in 94 per cent acetone. The large equivalent weight of iodobenzoic acid should make it an excellent precipitant for the quantitative determination of the alkaline earth metals. A study of this may be made at a later date.

Table I—Solubility of Alkaline Earth Halo-Benzoates in 94 Per Cent Acetone

(Expressed in millimoles per 100 cc.)

Halo-Benzoate	Calcium	Strontium	Barium
p-Cl	2.9	0.1	0.007
p-Br	1.79	0.028	less than 0.003
p-I	0.16	0.026	less than 0.003

Literature Cited

(1) Fresenius, *Z. anal. Chem.*, **82**, 189 (1893).
(2) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 490, Wiley, 1929.
(3) Rawson, *J. Soc. Chem. Ind.*, **16**, 113 (1897).

Electrolytic Determination of Cobalt[1]

Dorothy H. Brophy

Research Laboratory, General Electric Co., Schenectady, N. Y.

A rapid electrolytic method for the determination of cobalt has been described. This method makes use of a rapidly rotating anode (800 to 1000 r. p. m.), a gauze cathode, and an electrolytic solution consisting of ammonium chloride, ammonium hydroxide, and sodium bisulfite in amounts adjusted as described in the discussion.

By observing the recommended precautions, it is possible to remove from 15 to 160 mg. of cobalt in a half hour and obtain bright, adherent deposits in which the amount of sulfide has been reduced to a negligible quantity.

Organic acids, hydrazine sulfate or hydrochloride, and hydroxylamine hydrochloride have been tried under similar conditions and found to be unsatisfactory.

The use of cobalt in permanent magnets and cemented tungsten carbide brought about the necessity of a more rapid method for its determination. Electrolytic separations are always very attractive for rapid analyses, but have never been highly recommended for cobalt, possibly owing to the inability to reproduce results following suggested procedures. If a method required more than 1 hour, there was nothing gained over the present volumetric analysis now used (*5*). The object of this work has been to develop a rapid electrolytic determination of cobalt.

For the following experiments, Belgium cobalt was repurified by conversion to the chloropentamine cobalt chloride, dried and ignited to oxide, and reduced to metal by hydrogen-firing. The purity of the final product was determined by conversion to sulfate and ignition at 550° C. until constant weight had been obtained. The results thus obtained checked with the theoretical.

Stationary Electrodes

If stationary electrodes are used, two methods may be adopted. In one the solution may be stirred; in the other the electrolysis may be carried out in non-agitated solutions.

Electrolytic Solution

10 grams of $(NH_4)_2SO_4$
75 to 100 ml. of NH_4OH
Total volume, 100 ml.

This electrolytic solution served as a basis for the experiments. If the solutions were stirred, the electrolysis required from 6 to 7 hours. A current density of 3 amp. per sq. dm. was maintained and the electrodes were kept 4 cm. apart. A hemicylindrical cathode, 9 × 5 cm., with a wire anode was used for these experiments.

For non-agitated solutions, from 17 to 22 hours were required, and then one could not be sure of the complete removal of cobalt. A current density of 0.3 amp. per sq. dm. was maintained and the electrodes were kept about 2 cm. apart.

Results could not be reproduced using this electrolytic solution; modifying it by adding varying amounts of sodium bisulfite, acetic acid, formic acid, and oxalic acid did not improve results. Therefore, after about one hundred determinations the method was given up entirely.

Rotating Anode

A rotating anode has long been used for rapid electrolysis and was suggested and used for cobalt determinations by Smith and Kollock (*3*), Exner (*2*), Brenner and Ross (*1*), and Wagenman (*4*).

The apparatus used consisted of a rotating platinum anode and a platinum-rhodium gauze cathode. Attempts were made to reproduce the highly satisfactory results obtained by Smith and co-workers, but these attempts were unsuccessful. The deposits at times were very satisfactory and checked with the theoretical amounts of cobalt, but all the cobalt had not been removed from the solution. If complete deposition of cobalt were obtained, then the results were too high.

[1] Received April 15, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Hydrazine Sulfate Electrolytic Solution

30 ml. of NH_4OH
5 grams NH_4Cl
1 gram of $NH_2H_2N.H_2SO_4$ or HCl
Volume, 135 ml
CD_{100}, 3 to 6 amp.

This electrolytic solution was suggested by Wagenman, and looked very promising since the cobalt could be completely removed in 40 minutes. Results were always high to the extent of about 1 mg. The deposits looked quite fair. A second lot of hydrazine sulfate had to be used, and this proved to be very unsatisfactory, with very black deposits and results which were always high. At the suggestion of Doctor Fuess, Eastman Kodak Company, a small amount of gelatin was added to the new material. This amount was varied from 0.1 to 0.01 mg., and it did improve the character of the deposits, but the results were still 1 mg. high. Varying the amount of hydrazine, or gelatin, and boiling the gelatin with the reducing agent failed to give satisfactory results. The method was finally abandoned.

Hydroxylamine Hydrochloride

1 gram of K_2SO_4
40 ml. of NH_4OH
0.3 gram of $NH_2OH.HCl$
Volume, 100 ml.
CD_{100}, 4 to 7 amp.

This electrolytic solution was suggested by K. Dengg, formerly of the Ontario Cobalt Works (private communication to the author from H. H. Willard, University of Michigan). It proved unsatisfactory. No improvement in results was obtained by varying the amount of hydroxylamine, changing the sulfate solutions to chlorides, or adding a small amount of gelatin. The deposits were always black, powdery, and too high, and very seldom was all the cobalt removed in 1 hour.

Recommended Procedure

The most satisfactory electrolytic solution tried contained sodium bisulfite. This had been recommended for cobalt depositions, but has always carried with it the objection that sulfur is occluded in the deposits. Such procedures have called for the use of sulfate solutions and 1 to 2 grams of bisulfite. It seemed reasonable that if the amount of bisulfite and the time for electrolysis could be reduced, the error due to sulfur occlusion might be reduced to a negligible quantity or completely eliminated.

With this in mind, experiments were carried out with electrolytic solutions of varying compositions, and the following one was finally adopted:

Sodium Bisulfite Electrolytic Solution

50 ml. of NH_4OH
5 grams of NH_4Cl
0.3 to 0.4 gram of $NaHSO_3$
Volume, 80 to 100 ml.
800 to 1000 r. p. m.
CD_{100}, 4 to 7 amp.
Time, $^1/_2$ hour

The electrolyses were made in the solutions as soon as prepared. The bisulfite must be added to the alkaline solution. For amounts of cobalt from 100 to 160 mg., 0.3 gram of sodium bisulfite was needed. Less reducing agent gave streaked deposits and all the cobalt could not be removed in a half hour. For amounts of cobalt less than 100 mg.—that is, 80 mg. to 15 mg.—more bisulfite had to be used (0.4 gram) in order to get complete deposition in 30 minutes. Just why more reducing agent must be used with smaller amounts of cobalt is not quite clear, and until the function of the bisulfite is known, such a question cannot be answered. If the solution was not colorless in 20 minutes, 10 to 20 mg. more of bisulfite were added. In no case was it necessary to add 0.5 gram of reducing agent.

The rate of stirring is very important. If this falls below 800 r. p. m., deposits are darker and the electrolysis must be continued for more than a half hour. Such deposits always carry sulfur, and enough to give high results.

The addition of 0.1 to 0.5 mg. of gelatin to the electrolytic solution seemed to have a beneficial effect with small amounts of cobalt (80 to 15 mg.). The deposits had a better appearance and qualitatively carried less sulfur, although there is no difference in the quantitative results given in Table I.

Table I—Effect of Addition of Gelatin to Small Amounts of Cobalt

Gelatin	Cobalt Added	Cobalt Found	Error	Sulfur in Deposit
Mg.	*Mg.*	*Mg.*	*Mg.*	
0.1	12.5	12.9	+0.4	Trace
0.5	17.4	17.6	+0.2	None
0.5	31.3	31.5	+0.2	Trace
0.1	50.0	50.2	+0.2	Trace
None	59.2	5.9	+0.2	Trace
0.5	61.6	61.4	−0.2	None
None	71.3	71.4	+0.1	None
None	74.7	74.5	−0.2	Trace
0.5	80.7	80.7	00	None
None	82.3	82.3	00	Present
0.5	83.4	83.7	+0.3	Present
0.5	81.0	80.9	−0.1	Present
0.5	86.9	87.0	+0.1	Trace
0.1	88.1	87.9	−0.2	Present
None	100.1	100.4	+0.3	None
None	108.7	108.6	−0.1	None
None	111.6	111.9	+0.3	Trace
None	125.7	125.5	−0.2	Trace
None	134.0	133.3	−0.7	None
None	161.7	162.0	+0.3	None

After removing the deposit with dilute nitric acid and then boiling off most of the acid, the solutions were tested for sulfate with barium chloride. Complete removal of cobalt was assured by testing with phenylthiohydantoic acid (*5*).

The cathode tends to increase in weight. This was found to be owing to deposition of platinum dissolved from the anode, an error which can be taken care of by using the weight of the cathode after the cobalt has been removed for the calculations of results for that particular experiment. The increase in weight amounted to 0.2 mg. unless the electrolysis had been prolonged for three-quarters to one hour, when there was an increase of 0.5 mg.

It had been suggested that better deposits could be obtained by immersing the electrodes in the solution when the current was already on. This point was carefully tested and it was found that there was no difference in results if the electrodes were placed in the solution either before or after the current was applied.

Cobalt must be separated from any obviously interfering elements before electrodeposition. For this purpose, known amounts of cobalt were added to varying amounts of iron, and the cobalt precipitated with phenylthiohydantoic acid (*5*). The precipitate was washed and dried, ignited to oxide, and dissolved in concentrated hydrochloric acid. It may be dissolved in aqua regia and evaporated with concentrated sulfuric acid, although this process is less rapid. Potassium bisulfate fusions are not to be recommended, since the presence of sulfate necessitates a longer time for electrolysis. The last traces of iron must be removed by a double ammonium hydroxide precipitation.

Table II—Separation of Cobalt from Interfering Elements Using Iron

Iron as $Fe(NO_3)_3$	Cobalt Added	Cobalt Found	Error	Sulfur in Deposit
Mg.	*Mg.*	*Mg.*	*Mg*	
50	22.0	22.1	+0.1	None
50	20.5	20.5	00	None
100	27.0[a]	27.1	+0.1	None
500	21.4[a]	21.4	00	None
500	23.3	23.5	+0.2	None
1000	23.5[a]	23.7	+0.2	Trace
1000	23.8[a]	24.1	+0.3	None
1000	22.5[a]	22.5	00	None

[a] Phenylthio precipitate dissolved in hydrochloric plus nitric acids. For others ignited oxide dissolved in concentrated hydrochloric acid.

For the determination of cobalt in tungsten carbides, either the tungsten can be precipitated by conversion to tungsten

oxide or, if only the percentage of cobalt is desired, the cobalt may be precipitated directly with phenylthiohydantoic acid (*5*) and the electrolysis carried out as described in the discussion. Tools intended to contain from 13 to 14 per cent cobalt were found to have 13.81 and 13.83 per cent cobalt.

Acknowledgment

The author wishes to acknowledge the coöperation of Charles Van Brunt and Margaret O. St. Louis of this department; also Roger L. Jones, of Syracuse University, who spent last summer in this laboratory.

Literature Cited

(1) Brenner and Ross, *J. Am. Chem. Soc.*, **33**, 493 (1911).
(2) Exner, *Ibid.*, **25**, 896 (1903).
(3) Smith and Kollock, *Ibid.*, **26**, 1595, 1606 (1904); **27**, 1255 (1905).
(4) Wagenman, *Metall Erz*, **18**, 447 (1921).
(5) Willard and Hall, *J. Am. Chem. Soc.*, **44**, 2219 (1922).

A Test for Aldehydes Using Dimethylcyclohexanedione[1]

Woltor Weinberger

THE MENNEN COMPANY, NEWARK, N. J.

THIS valuable test, since its introduction by Vorlander in 1896 (*5, 7*), has been neglected by and is still unknown to the majority of chemists. Of late it has been infrequently used in work in photosynthesis and in detecting traces of aldehydes in biological material, but it has never received the place it deserves as a routine and definite test for aldehydes.

There are several distinct advantages inherent in this test: (1) reliability; (2) sensitivity; (3) definiteness (it yields a crystalline precipitate); (4) simplicity of technic; (5) a reagent which does not react with ketones; and (6) which can often be used when other better known reagents cannot give the information sought.

Its chief disadvantage, formerly, was that the reagent was not readily available. It may now be purchased easily from the Eastman Kodak Company, Rochester, N. Y.

The reagent is dimethylcyclohexanedione, commonly called dimetol and dimethylhydroresorcin. It unites with aldehydes, the condensation product so formed being soluble in water with difficulty.

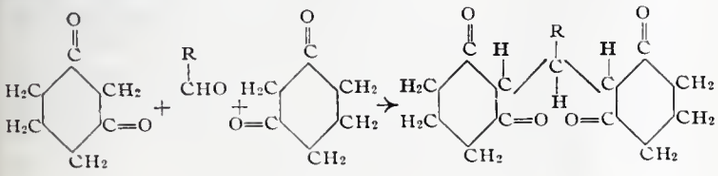
The result of work undertaken to determine how this reagent might best be used, its defects, and its sensitivity, is here presented. The melting points of a number of derivatives are also included. The original experiments were performed with formaldehyde. Subsequent experiments, however, show that the method adopted and the conditions and cautions laid down here apply equally well to other aldehydes.

The reagent is soluble in alcohol and water. It oxidizes slowly in the presence of air, and when kept in well-stoppered bottles keeps indefinitely (*6*).

Test Procedure

The solution of the reagent is added to the solution of the aldehyde. Under proper conditions the condensation product separates out of the solution as a fine crystalline and exceedingly insoluble precipitate.

The oxygen of one molecule of formaldehyde unites with a hydrogen atom of each of two molecules of the reagent, water splitting off, and the residue is the insoluble compound (*4, 5, 7*). Let us assume for the sake of simplicity that the reagent is dihydroresorcin



This condensation product is soluble in hot water, alcohol ether, petrolic ether, gasoline, acetone, and, very probably, in most organic solvents. It is essential as a first condition, then, that the aldehyde be precipitated from a cold aqueous solution, although small amounts of alcohol do not interfere. It may be noted here that the condensation can take place in an alcoholic solution and the condensation product precipitated by the addition of water. These solubilities in hot water and in alcohol are put to good use in purifying the crystals for melting-point determinations.

The condensation product is easily soluble in fixed and carbonate alkalies and in acids, but it is not appreciably soluble in cold, very dilute solutions of organic acids. The reagent should, therefore, be added to a neutral solution of the aldehyde. Since this is impracticable, the solution of the aldehyde should be made faintly acid with some weak organic acid.

A saturated aqueous solution of the condensation product formed by the reaction of formaldehyde and dimetol contains at 19° C. 0.0005 gram per 100 ml. (*6*), and much less than that in the presence of excess dimetol. The condensation product is still less soluble in the presence of salt. The addition of sodium chloride was resorted to in order to increase the sensitivity of the test.

The precipitate does not come immediately, but comes down slowly, becomes bulkier on standing, and then takes its final crystalline form. The formation of the precipitate and its crystallization is materially hastened by vigorous stirring. This precipitate shows a characteristic structure under the microscope (*3*).

Method for Precipitation of Aldehydes

The method decided upon for the precipitation of aldehydes by dimetol is as follows:

A 5 to 10 per cent alcoholic solution of the reagent is prepared.
Sodium chloride is added to the aqueous solution of the aldehyde.
The aqueous solution containing the aldehyde is neutralized and left neutral or very faintly acid—e. g., with dilute acetic acid—and cooled.
To this cold solution a few drops of the reagent are added.
The solution is then vigorously stirred, or permitted to stand until the precipitate takes its final crystalline form.

The precipitate may be recrystallized from a suitable solvent (for example, alcohol or hot water), and its melting point determined. By means of this determination the presence of a specific aldehyde may be confirmed. A number of melting points for dimetolaldehyde derivatives and their sources are given in Table I.

[1] Received May 26, 1931.

It is worth mentioning here that dimetol gives no precipitate with ketones, so that it may be used to determine aldehydes in the presence of ketones.

Sensitivity of Test

A solution containing 4 mg. of formaldehyde per liter gives a definite precipitate in 15 minutes, using salt. This degree of sensitivity was determined as follows:

A number of formaldehyde solutions properly neutralized and of various strengths were prepared, sodium chloride was added to each, and they were all kept at 25° C. To a portion of each solution a few drops of the reagent were added, and the weakest concentration of formaldehyde that gave a definite precipitate within 15 minutes was taken as the limit of the sensitivity of the test. The time limit was set because it was desired that the test be used as a rapid test and in routine analysis. Long waiting would, obviously, have made it unfit for such a purpose.

Under the conditions stated, formaldehyde was definitely detected in a solution containing only four parts of formaldehyde per million.

Because of its extreme sensitivity, the definiteness of the precipitate, and the very simple technic required, this test should rank high among the classic tests for aldehydes. That it may be put to a wider use, notably in differentiating between and in confirming the presence of certain specific aldehydes, the melting points of the condensation products formed by the reaction of dimetol and certain aldehydes are described (Table I). It is hoped that this list may be expanded in time.

Table I—Melting Points of Condensation Products of Dimetol and Various Aldehydes

Aldehyde	Melting Point
	° C.
Formaldehyde	187
Acetaldehyde	138 to 140 (*4*)
Anhydride of acetaldehyde	173 to 175 (*4*)
Citral	approx. 25
Citronellal	70 to 71 (*1*)
Anisic aldehyde	142 (*1*)
Acetylvanillin	167 (*1*)
Piperonal	193 (*2*)
Vanillin	196 (*2*)
Salicylic aldehyde	208 to 209

Literature Cited

(1) Bernardi, *Ann. chim. applicata*, **17**, 163 (1927).
(2) Bernardi and Tartarini, *Ibid.*, **16**, 132 (1926).
(3) Leffman and Pines, *Bull. Wagner Free Inst. Sci. Phila.*, **4**, 15 (1929).
(4) Stepp and Feulgen, *Z. phys. Chem.*, **114**, 301 (1921).
(5) Vorlander, *Ber.*, **30**, 1801 (1897).
(6) Vorlander, *Ibid.*, **58B**, 2656 (1925).
(7) Vorlander and Kalkow, *Ann. chim.*, **39**, 356 (1899).

Method for Determination of Fluorine in Phosphate Rock and Phosphatic Slags[1]

D. S. Reynolds and K. D. Jacob

Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

The fluorine in highly phosphatic, calcareous materials, such as phosphate rock, cannot be brought into the water-soluble condition by a single fusion with alkaline fluxes. Three fusions usually fail to convert more than about 90 per cent of the fluorine into the water-soluble condition. The failure of alkaline fusions to effect complete decomposition of such materials is due to the setting up of equilibrium reactions involving insoluble fluorphosphates of the fluorapatite type.

A method for the determination of fluorine in phosphate rock and phosphatic slags is described. The method involves a single fusion of the sample with sodium carbonate and silica, followed by extraction of the water-insoluble residue with dilute nitric acid. After removal of the dissolved calcium and phosphoric acid, the fluorine is determined by the lead chlorofluoride method. The method gives satisfactory results on fluorine-bearing phosphatic slags and on the domestic types of phosphate rock with the exception of Tennessee blue-rock phosphate. Comparative results are given for fluorine in various phosphatic materials, as determined by this method and by the volatilization method.

In an investigation of the volatilization of fluorine during the smelting of phosphate rock it was necessary to determine the fluorine content of slags containing various quantities of phosphate. Preliminary studies showed that the volatilization method (*12*, *16*), which is widely used for the determination of fluorine in phosphate rock, gives very low and erratic results when applied to the analysis of fluorine-bearing slags, such as those obtained in the manufacture of phosphoric acid by furnace processes. The low results obtained with this method may be due in part to failure of the sulfuric acid to effect complete decomposition of the fluorine compounds present in the slag. The principal source of error seems to lie, however, in the formation of a non-volatile oxyfluoride, probably $SiOF_2$ (*1*), by the action of hydrofluoric acid on the silicic acid resulting from the action of sulfuric acid on silicates present in the slag.[2] It seemed necessary, therefore, to resort to some method involving alkali fusion in order to determine fluorine in the slags. At the same time it was desired to obtain, if possible, a method that would be applicable also to the determination of fluorine in phosphate rock, inasmuch as the volatilization method, under the most favorable conditions, seems to give a recovery of only about 92 to 94 per cent of the fluorine present in this material (*12*).

The lead chlorofluoride method, first suggested by Starck (*14*) and later studied in some detail by Hawley (*4*), has recently been applied by Hoffman and Lundell (*6*, *7*) to the determination of fluorine in glasses and enamels, with excellent results. Hoffman and Lundell state, however, that the method as developed by them is not suitable for determining fluorine in phosphate rock. This was confirmed by the writers in several experiments, only about one-half of the fluorine being recovered. It seemed desirable, however, to make a further study of the method to determine whether it might be modified to give satisfactory results on phosphatic materials. After considerable experimental work a modification was developed which seems to give fairly satisfactory results for fluorine in phosphate rock and phosphatic slags. The results of this study are given in the present paper.

[1] Received May 14, 1931. Presented before the Division of Fertilizer Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

[2] See the immediately following paper, "Effect of Certain Forms of Silica on Determination of Fluorine by Volatilization Method."

Preliminary Experiments

The method as outlined by Hoffman and Lundell is designed for the determination of fluorine and silica on the same sample. Briefly it is as follows:

The sample is fused with sodium or potassium carbonate and the insoluble residue remaining from the disintegration of the melt with hot water is filtered off. Silica is removed from the filtrate by two precipitations, first with acid zinc nitrate solution, and second with ammoniacal zinc oxide solution. The filtrate from the second silica precipitation is treated with hydrochloric acid, lead nitrate, and sodium acetate to precipitate lead chlorofluoride (PbClF), and the chlorine in the latter is determined volumetrically by means of standard silver nitrate and potassium thiocyanate solutions.

Preliminary experiments showed that the low results obtained on phosphatic materials by the Hoffman and Lundell procedure are due to interference of the phosphate. It was thought that the trouble lay either in the lead chlorofluoride precipitation or in the alkali fusion.

In order to obtain information on the effect of phosphate on the lead chlorofluoride precipitation, various quantities of phosphoric acid in the form of potassium dihydrogen phosphate were added to solutions containing 8 grams of sodium nitrate (equivalent to 5 grams of sodium carbonate) and 0.040 gram of fluorine as sodium fluoride. The Hoffman-Lundell procedure was followed in precipitating the lead chlorofluoride and determining the fluorine equivalent of the chlorine. In the absence of phosphoric acid, 0.0401 gram of fluorine was found, whereas in the presence of 0.005 to 0.06 gram of phosphoric acid (P_2O_5), the quantities of fluorine found increased progressively from 0.0407 gram to 0.0467 gram. As pointed out by Hawley (*4*), the high results in the presence of phosphates are probably due to the fact that when lead phosphate is precipitated in the presence of chlorides, it carries with it some lead chloride.

Since it is evidently necessary to remove phosphate prior to the lead chlorofluoride precipitation, experiments were carried out to determine whether the two zinc treatments used by Hoffman and Lundell for precipitating silica[3] are effective also in removing the phosphate. A solution containing 0.040 gram of fluorine as sodium fluoride, 0.35 gram of phosphoric acid (P_2O_5), and 5 grams of sodium carbonate was carried through the zinc precipitations and the subsequent operations outlined by Hoffman and Lundell, with a recovery of 0.0402 gram of fluorine. Only about 0.005 gram of phosphoric acid remained in the solution after the zinc treatments. In a second experiment, 1 gram of silica was fused with 10 grams of sodium carbonate and the melt was dissolved in a solution containing 0.040 gram of fluorine and 0.35 gram of phosphoric acid. About 0.008 gram of phosphoric acid remained in solution after the zinc treatments and 0.0398 gram of fluorine was recovered.

These results show that the zinc treatments correct the error arising from the presence of phosphates in solution. They indicate also that the low results obtained on phosphatic materials are due to failure of the alkali fusion to convert all the fluorine into a water-soluble condition. This was shown to be the case in a number of experiments with various fusion mixtures.

Alkali Fusion of Fluorine-Bearing Phosphatic Materials

Bureau of Standards standard sample No. 56, Tennessee brown-rock phosphate, was used in the majority of the experiments with different fusion mixtures. Previous analyses (*11*) of this material by the volatilization method, together with analyses during the present investigation, indicate that it contains between 3.45 and 3.55 per cent fluorine. For the purpose of the present paper a fluorine value of 3.45 per cent is used. Several experiments were also made with synthetic mixtures of tricalcium phosphate and Bureau of Standards fluorspar, standard sample No. 79, containing 46.19 per cent fluorine. The carbonate fusions were made in platinum dishes in a muffle furnace at 950° C. for one hour. The sodium hydroxide fusions were made in nickel crucibles at 600° C. for one hour. The sodium peroxide–carbon fusions were made in nickel crucibles according to the recommendations of Muehlberg (*10*), and Marvin and Schumb (*8*).

The results given in Table I show that only 50 to 60 per cent of the fluorine was recovered from phosphate rock by a single fusion with sodium carbonate, sodium carbonate plus potassium carbonate, or sodium hydroxide. The sodium peroxide–carbon fusions also gave poor results. Addition of silica had a beneficial effect, but even then a maximum of only about 82 per cent of the fluorine was recovered. Similar results were obtained on mixtures of fluorspar and either dicalcium or tricalcium phosphate.

Table I—Recovery of Fluorine by Single Fusion with Various Fusion Mixtures

Material	Fusion Mixture	Fluorine Present	Fluorine Recovered	
		Mg.	*Mg.*	%
Tennessee brown-rock phosphate,[a] 1 g.	2 g. Na_2CO_3	34.5	17.5	50.7
	10 g. Na_2CO_3	34.5	20.4	59.1
	4.5 g. Na_2CO_3 + 5.5 g. K_2CO_3	34.5	18.4	53.3
	1 g. Na_2CO_3 + 0.5 g. SiO_2[b]	34.5	16.9	49.0
	2 g. Na_2CO_3 + 0.5 g. SiO_2	34.5	28.2	81.7
	3 g. Na_2CO_3 + 0.5 g. SiO_2	34.5	26.1	75.7
	4 g. Na_2CO_3 + 0.5 g. SiO_2	34.5	26.5	76.8
	8 g. Na_2CO_3 + 0.5 g. SiO_2	34.5	26.6	77.1
	2 g. Na_2CO_3 + 0.25 g. SiO_2	34.5	23.3	67.5
	2 g. Na_2CO_3 + 0.75 g. SiO_2	34.5	28.2	81.7
	7 g. NaOH	34.5	21.1	61.2
	7 g. NaOH + 0.5 g. SiO_2	34.5	28.2	81.7
	15 g. Na_2O_2 + 0.9 g. C	34.5	16.8	48.7
	15 g. Na_2O_2 + 0.9 g. C + 0.5 g. SiO_2	34.5	24.9	72.2
Tennessee brown-rock phosphate,[a] 0.5 g.	6 g. Na_2CO_3 + 0.75 g. feldspar	17.25	14.1	81.7
$Ca_3(PO_4)_2$, 0.7 g. + CaF_2,[c] 0.0821 g.	2 g. Na_2CO_3 + 0.5 g. SiO_2	37.9	23.8	62.8
$CaHPO_4$, 0.73 g. + CaF_2,[c] 0.0821 g.	2 g. Na_2CO_3 + 0.5 g. SiO_2	37.9	27.4	72.3
$CaHPO_4$, 0.5 g. + CaF_2,[c] 0.05 g.	6 g. Na_2CO_3 + 0.75 g. feldspar	23.1	15.3	66.2
Electric furnace slag, 1 g.	5 g. Na_2CO_3	35.7[d]	31.0	86.8

[a] Bureau of Standards standard sample No. 56, containing 9.26 per cent of SiO_2.
[b] In all cases SiO_2 in fusion mixture is in addition to that present in phosphatic material.
[c] Fluorspar, Bureau of Standards standard sample No. 79.
[d] Approximate figure.

Fairchild (*3*) states, in a recent paper, that the fluorine in a mixture of dicalcium phosphate and fluorspar is completely converted into the water-soluble condition by fusion with a mixture of sodium carbonate and feldspar. The writers were unable, however, to confirm Fairchild's statement. The figures given in Table I show that sodium carbonate–feldspar fusions gave no better results on either phosphate rock or mixtures of dicalcium phosphate and fluorspar than those obtained by sodium carbonate–silica fusions. (The phosphate rock and feldspar were ground to 200 mesh.) Fairchild's conclusion that all the fluorine is brought into the water-soluble condition by a single fusion with sodium carbonate and feldspar is based upon his failure to find fluorine in the insoluble residue by the etching and hanging drop tests. It is known, however, that these tests (*1*, *15*) are not reliable in the presence of amorphous silica, silicic acid, or silicates which are easily decomposed by sulfuric acid. The insoluble residue from the sodium carbonate–feldspar fusion of the mixture of dicalcium phosphate and fluorspar did not give a test for fluorine by the etching test, and the results by the hanging drop test were questionable, despite the fact that the residue actually contained approximately 0.008 gram of fluorine.

[3] According to Hawley, silica itself does not interfere in the determination of fluorine by the lead chlorofluoride method.

The figures given in Table II show that, in general, three successive fusions did not bring into the water-soluble condition all the fluorine present in phosphate rock and in synthetic mixtures of tricalcium phosphate and fluorspar. It seems that, in general, less than 90 per cent of the fluorine can be recovered in this way, although a 99 per cent recovery was obtained in one case. The results give further evidence of the beneficial effect of silica in the fusion mixture.

Table II—Recovery of Fluorine by Three Successive Fusions with Various Fusion Mixtures

Material	Fusion Mixture	Fluorine Present	Fluorine Total recovered	
		Mg.	*Mg.*	%
Tennessee brown-rock phosphate,[a] 1 g.	2 g. Na_2CO_3	34.5	26.0	75.4
	4.5 g. Na_2CO_3 + 5.5 g. K_2CO_3	34.5	22.9	66.4
	2 g. Na_2CO_3 + 0.5 g. SiO_2[b]	34.5	34.4	99.7
Florida pebble phosphate,[c] 1 g.	2 g. Na_2CO_3 + 0.5 g. SiO_2	37.8[d]	32.8	86.8
$Ca_3(PO_4)_2$, 0.83 g. + CaF_2,[e] 0.0836 g.	2 g. Na_2CO_3 + 0.5 g. SiO_2	38.6	33.9	87.8
$Ca_3(PO_4)_2$, 0.73 g. + CaF_2,[e] 0.0821 g.	2 g. Na_2CO_3 + 0.5 g. SiO_2	37.9	33.3	87.9

[a] Bureau of Standards standard sample No. 56.
[b] In all cases, SiO_2 in fusion mixture is in addition to that present in phosphatic material.
[c] Representative sample of commercial material.
[d] Approximate figure.
[e] Fluorspar, Bureau of Standards standard sample No. 79.

Reactions Occurring in Alkali Fusion of Phosphates

When identical fusion mixtures were used, for example, 2 grams of sodium carbonate and 0.5 gram of silica, duplicate determinations on a particular sample of phosphate rock, or mixture of tricalcium phosphate and calcium fluoride, usually checked within 0.001 gram of fluorine, despite the fact that, in general, complete recovery of the fluorine was not obtained even with three successive fusions. Almost identical results were obtained when the determinations were repeated at a later date. Calcium fluoride alone is completely converted into the water-soluble condition by a single fusion with sodium carbonate and silica, but mixtures of calcium fluoride and calcium phosphate behave like phosphate rock.

These facts indicate that in the alkali fusion of fluorine-bearing phosphatic materials, failure to obtain all the fluorine in the water-soluble condition, even after repeated fusion, is due to equilibrium reactions in the melt involving a water-insoluble fluorine-phosphate compound. It seems to be definitely established that the fluorine in phosphate rock is present principally in the form of a complex calcium fluorphosphate having the same empirical formula, $3Ca_3(PO_4)_2.CaF_2$, as crystalline fluorapatite. A number of investigators (*9*) have prepared this compound by heating mixtures of calcium fluoride and calcium phosphate in the presence of alkali salts.

A further study of the reaction showed that alkali fusion, with or without addition of silica, does not convert the same percentages of the total phosphoric acid and total fluorine into the water-soluble condition. In one experiment, fusion of 1 gram of phosphate rock with 10 grams of sodium carbonate converted 60 per cent of the fluorine and only 32 per cent of the phosphoric acid into the water-soluble condition. A second fusion solubilized 28 per cent of the remaining fluorine and 11 per cent of the remaining phosphoric acid. These inequalities may result from the formation of water-insoluble calcium sodium phosphate, $CaNaPO_4$ (*2, 13*), but further investigation of the conditions under which this compound is formed are necessary before a definite statement to that effect can be made.

With these facts in mind, the principal reaction occurring when phosphate rock is fused with pure sodium carbonate, under the customary conditions, may be represented, for the present, by the equation

$$3Ca_3(PO_4)_2.CaF_2 + 10Na_2CO_3 \rightleftharpoons 10CaCO_3 + 6Na_3PO_4 + 2NaF$$

In the presence of silica, the reactions may be represented by the equation

$$3Ca_3(PO_4)_2.CaF_2 + 10SiO_2 + 10Na_2CO_3 \rightleftharpoons 10CaSiO_3 + 6Na_3PO_4 + 2NaF + 10CO_2$$

Similar reactions occur in the fusion of fluorine-bearing phosphatic slags and of synthetic mixtures of calcium phosphates and calcium fluoride.

Acid Extraction of Fluorine from Fusion Residues

Inasmuch as satisfactory extraction of the fluorine did not seem to be possible by alkali fusion alone, experiments were made to determine whether the fluorine remaining in the insoluble residue from a single alkali fusion could be extracted by treatment with dilute acid. It was found that complete extraction of the fluorine could be obtained by treating the residue with nitric acid (1 to 10). The acid treatment introduces, however, several complications. In the first place, the calcium that is brought into solution simultaneously with the fluorine must be removed in order to prevent loss of fluorine as calcium fluoride during the zinc precipitations. This may be accomplished by precipitation as calcium oxalate under carefully controlled conditions. It is very difficult to obtain fluorine-free precipitates of calcium oxalate if more than about 20 mg. of fluorine are present.

It is then necessary to remove the excess of oxalic acid remaining in the filtrate from the calcium oxalate precipitate. If this is not done, the oxalate is carried into the lead chlorofluoride precipitate as lead oxalate and makes it impossible to obtain a satisfactory end point in the thiocyanate titration. This is effected by oxidation with potassium permanganate in slightly acid solution, and the manganese is precipitated as a mixture of the phosphate, carbonate, and dioxide by treatment with sodium carbonate. The filtrate from the manganese precipitate is then added to the solution obtained by water extraction of the melt resulting from the alkali fusion of the original material. The method used for the final determination of fluorine is essentially the same as that described by Hoffman and Lundell. Direct treatment of phosphate rock with dilute nitric acid was quite effective in bringing the fluorine into solution, but the final results were erratic and usually much lower than those obtained by the combination of alkali fusion and acid extraction.

Recovery of Fluorine in Presence of Pyrite and Calcium Sulfate

According to Hawley (*4*), the presence of 0.1 gram of iron sulfide (FeS_2) causes a serious reduction in the recovery of fluorine from fluorspar by fusion methods. Hawley's results indicate that this loss is reduced but is not entirely prevented by oxidizing the sulfide with a small quantity of sodium peroxide or potassium nitrate.[4] Hoffman and Lundell (*7*), on the other hand, did not find a significant loss of fluorine when 10 per cent of iron sulfide (FeS_2) was added to an opal glass containing 5.75 per cent fluorine.

Some types of phosphate rock, particularly Tennessee blue-rock, contain appreciable quantities of iron sulfide, principally pyrite, and acid-soluble sulfate, principally gypsum. Inasmuch as the fusion–acid extraction method in the absence of oxidizing agents gave results appreciably lower than those obtained by the volatilization method on several samples of Tennessee blue-rock phosphate (Table IV) experiments were made to determine whether better recovery could be obtained in the presence of oxidizing agents such as potassium nitrate and sodium peroxide. In making these experiments the 200-mesh materials were thoroughly mixed with

[4] Hawley does not state whether the oxidation of the sulfide was carried out prior to or simultaneously with the fusion of the sample.

the fusion mixture and oxidizing agent, and the oxidation and fusion were carried out simultaneously. The fusion–acid extraction method, as outlined later, was used.

The results given in Table III show that when no oxidizing agent was used, addition of 0.1 gram of pyrite or of gypsum had no pronounced effect on the recovery of fluorine from mixtures of tricalcium phosphate and fluorspar. The addition of 0.1 gram of potassium nitrate had no effect on the recovery of fluorine from mixtures containing only tricalcium phosphate and fluorspar, but in the presence of 0.1 gram of pyrite, the recovery from synthetic mixtures was seriously reduced by the use of either potassium nitrate or sodium peroxide as oxidizing agents. In the case of the Tennessee blue-rock phosphate No. 930, however, addition of 0.1 gram of oxidizing agent gave, in general, a significant increase in the recovery of fluorine, but the results were still lower than those obtained by the volatilization method. This particular sample contained 5.18 per cent of SO_3 in the form of acid-insoluble sulfide. The addition of 0.1 gram of potassium nitrate did not improve the recovery of fluorine from Tennessee brown-rock phosphate, Bureau of Standards sample No. 56, which contained 1.18 per cent of SO_3 as acid-insoluble sulfide.

Table III—Recovery of Fluorine in Presence of Pyrite and Calcium Sulfate

Material	Oxidizing Agent[a]	Fluorine Recovered
		Mg.
$Ca_3(PO_4)_2$, 0.7 g. + CaF_2,[b] 0.0821 g. (37.9 mg. F)	None	36.9
	0.1 g. KNO_3	37.6
	0.1 g. KNO_3	36.5
	0.1 g. KNO_3	36.2
$Ca_3(PO_4)_2$, 0.7 g. + CaF_2, 0.0821 g. + gypsum, 0.1 g. (37.9 mg. F)	None	35.9
	None	36.3
$Ca_3(PO_4)_2$, 0.7 g. + CaF_2, 0.0821 g. + FeS_2,[c] 0.1 g. (37.9 mg. F)	None	37.1
	None	36.7
	0.1 g. KNO_3	33.5
	0.1 g. KNO_3	35.9
	0.1 g. Na_2O_2	34.4
	0.1 g. Na_2O_2	34.9
$Ca_3(PO_4)_2$, 0.7 g. + CaF_2, 0.0821 g. + FeS_2, 0.050 g. + gypsum, 0.050 g. (37.9 mg. F)	None	31.7
	None	35.4
	0.1 g. KNO_3	34.8
	0.1 g. KNO_3	36.0
Tennessee blue-rock phosphate,[d] No. 930, 1 g. (> 35.3 mg. F)	None	31.9
	None	32.1
	0.1 g. KNO_3	34.3
	0.1 g. KNO_3	33.5
	0.1 g. Na_2O_2	33.9
	0.1 g. Na_2O_2	32.2
	0.2 g. Na_2O_2	33.0
	0.2 g. Na_2O_2	33.8
	0.3 g. KNO_3	33.0
	0.3 g. Na_2O_2	31.4
Tennessee brown-rock phosphate,[e] Bureau of Standards No. 56, 1 g. (34.5 mg. F)	None	33.4
	None	32.9
	0.1 g. KNO_3	30.3
	0.1 g. KNO_3	32.8
Florida pebble phosphate,[f] 1 g. (> 36.8 mg. F)	None	36.4
	None	36.0
	0.1 g. KNO_3	35.5
	0.1 g. KNO_3	36.5

[a] Fusion mixture of 2 grams of Na_2CO_3 + 0.5 gram of SiO_2 used in all experiments.
[b] Fluorspar, Bureau of Standards standard sample No. 79.
[c] Crystalline pyrite.
[d] Containing total SO_3, 6.61 per cent; acid-soluble sulfate, 1.25 per cent SO_3; and acid-insoluble sulfide, 5.18 per cent SO_3.
[e] Containing total SO_3, 2.82 per cent; acid-soluble sulfate, 1.23 per cent SO_3; and acid-insoluble sulfide, 1.18 per cent SO_3.
[f] Containing total SO_3, 0.30 per cent; acid-soluble sulfate, 0.20 per cent SO_3; and acid-insoluble sulfide, 0.00 per cent SO_3.

Experiments were also made with synthetic mixtures of tricalcium phosphate, calcium fluoride, pyrite, and gypsum. In the absence of an oxidizing agent, low and erratic results were obtained. When 0.1 gram of potassium nitrate was added to the fusion mixture, the results were more consistent but were still lower than those obtained by the volatilization method. This indicates that the low figures obtained on Tennessee blue-rock phosphate are caused by a reaction, or reactions, involving the gypsum, pyrite, and calcium fluoride, or calcium fluorphosphate, present in the rock. Roasting at temperatures up to 800° C. prior to fusion with sodium carbonate did not improve the recovery of fluorine from Tennessee blue-rock phosphate. The results, as a whole, indicate that, with the possible exception of Tennessee blue-rock phosphate, the recovery of fluorine from phosphatic materials is not improved by the addition of an oxidizing agent to the fusion mixture.

Special Reagents Used in Method

Silica—Any type of anhydrous fluorine-free silica may be used. It should be ground to 200 mesh.

Acid Zinc Nitrate—Dissolve 5 grams of zinc oxide in 100 ml. of dilute nitric acid (1 to 9).

Ammoniacal Zinc Oxide—Dissolve 10 grams of ammonium carbonate in 100 ml. of water and 10 ml. of ammonium hydroxide (sp. gr. 0.90). Add 5 grams of zinc oxide and heat on the steam bath until a clear solution is obtained, adding more ammonia if necessary.

Bromophenol Blue Indicator—Prepare a 0.4 per cent solution by grinding the dry powder with sodium hydroxide solution (1.5 ml. of 0.1 *N* sodium hydroxide to 0.1 gram of powder) and diluting to the proper volume.

Lead Nitrate—It is the writers' experience that the use of the so-called c. p. grades of lead nitrate may lead to low results for fluorine, particularly if the salt has been dried at too high a temperature or for too long a time at a lower temperature. It is advisable to test the salt by using it to precipitate lead chlorofluoride from a solution of sodium fluoride of known purity. If the results for fluorine are too low, the lead nitrate should be recrystallized from a solution containing 2 ml. of concentrated nitric acid to 100 ml. of water. Dry the recrystallized salt at a temperature below 100° C. and determine its behavior towards a solution of sodium fluoride of known purity.

Lead Chlorofluoride Wash Solution—(*a*) Dissolve 10 grams of lead nitrate in 200 ml. of water. (*b*) Dissolve 1 gram of sodium fluoride in 100 ml. of water and add 2 ml. of concentrated hydrochloric acid. Mix solutions *a* and *b*, allow the precipitate to settle, decant the supernatant liquid, and wash the precipitate 4 or 5 times with 200 ml. of water by decantation. Transfer the precipitate to a large beaker or flask, add about 1 liter of cold water, and allow to stand for 1 hour or longer with occasional stirring. Filter and keep the clear filtrate for use as a wash solution. Save the remainder of the precipitate for the preparation of further quantities of wash solution as needed.

0.1 *N* Silver Nitrate—It is preferable to standardize this solution by precipitating and weighing the chlorine as silver chloride. One milliliter of 0.1 *N* solution is equivalent to 0.00190 gram of fluorine.

Ferric Alum Indicator—Prepare a saturated solution (free from chlorides) and add a few milliliters of concentrated colorless nitric acid to bleach the brown color.

0.1 *N* Potassium Thiocyanate—Standardize this solution against the silver nitrate solution.

Procedure

Grind the sample to a fineness of about 100 mesh. In the case of phosphate rock, fuse a 1-gram sample in a platinum crucible or dish with 2 grams of sodium carbonate and 0.5 gram of silica[5] at a temperature of 900° to 950° C. for 1 hour. In the case of slags containing a considerable quantity of silicates, fuse a 1-gram sample with 5 grams of sodium carbonate. Transfer the cooled melt to a beaker, digest overnight on the steam bath with 50 to 75 ml. of water, and decant the solution onto a filter. Break up the lumps thoroughly with the stirring rod and digest with 50 ml. of a 1 or 2 per cent sodium carbonate solution on the steam bath for about 15 minutes with frequent stirring. Filter into a 400-ml. beaker, wash the residue 5 or 6 times with hot water, and evaporate the combined filtrates to a volume of 50 to 75 ml. This solution, *A*, which contains the greater portion of the fluorine, is reserved for further treatment.

By means of a jet of warm water return the residue to the same beaker in which the water and carbonate digestions were made, using a total volume of about 50 ml., add 3 ml. of concentrated nitric acid, and allow the mixture to stand for 0.5

[5] In the case of Tennessee blue-rock phosphate somewhat higher results are obtained by the addition of 0.1 gram of potassium nitrate or sodium peroxide to the fusion mixtures. The nitrate is preferable because it is easier to handle.

to 1.0 hour with frequent stirring. This treatment will usually bring all the fluorine into solution, but in case considerable insoluble material remains, it is advisable to filter it off, fuse with a small amount of sodium carbonate, and add the water extract of the melt to solution *A*. Add 50 ml. of a 5 per cent oxalic acid solution to the cold nitric acid solution and precipitate calcium oxalate by adding 10 per cent sodium carbonate solution drop by drop until the solution is neutral to methyl orange. Boil the mixture 1 minute, stirring continuously to prevent bumping, and after cooling, filter and wash the precipitate four or five times with cold water. Make the filtrate acid to methyl orange, add 4 ml. of concentrated nitric acid and 10 ml. of saturated potassium permanganate solution, and warm on a hot plate or steam bath. When the color disappears, add more permanganate solution drop by drop until the solution becomes permanently colored, or a brown precipitate forms. Neutralize the excess acid by adding solid sodium carbonate in small quantities until frothing ceases, and then add about 2 grams of carbonate in excess. If the precipitate is light colored, add permanganate solution drop by drop until it becomes dark brown, and bring the mixture to boiling, stirring continuously. Filter the hot solution through a rapid-filtering 12.5- or 15-cm. paper and wash the precipitate four or five times with a hot 1 per cent sodium carbonate solution. Catch the filtrate in the beaker containing solution *A* and adjust the volume to about 250 ml. The procedure from this point is essentially the same as that recommended by Hoffman and Lundell.

Heat the solution to boiling, add 25 ml. of acid zinc nitrate solution, and bring to a boil, stirring continuously to prevent bumping. The precipitate is very heavy and loss of the determination is almost certain to occur unless bumping is prevented. Filter through a rapid-filtering 15-cm. paper into a 600-ml. beaker, wash to a volume of about 400 ml., and discard the precipitate. Neutralize the solution with nitric acid, using methyl red as an indicator and heating almost to boiling before the final end point is reached, add 25 ml. of ammoniacal zinc oxide solution, and evaporate to a volume of 50 to 75 ml. Wash down the side of the beaker with 50 ml. of warm water, allow to stand until the precipitate settles, and then filter and wash with cold water to a volume of 250 ml. Discard the precipitate. Add 2 drops of bromophenol blue indicator to the solution, make slightly acid with dilute nitric acid and then just alkaline with dilute sodium hydroxide, and add 3 ml. of a 10 per cent sodium chloride solution and 2 ml. of dilute hydrochloric acid (1 to 1). Add 5 grams of solid lead nitrate and heat on the steam bath. After the lead nitrate has completely dissolved, add 5 grams of solid sodium acetate, and heat on the steam bath for 0.5 hour with occasional stirring. Allow the solution and precipitate to stand for 4 hours or overnight at room temperature, and filter through a paper of close texture. Wash the precipitate, beaker, and paper once with cold water, then four or five times with a cold saturated solution of lead chlorofluoride, and finally once more with cold water.

Transfer the precipitate and paper to the beaker in which the precipitation was made, wash the precipitate from the paper with 100 cc. of dilute nitric acid (1 to 19), warm until the precipitate is dissolved,[6] and then pulp the filter paper in the solution. Add a slight excess of 0.1 *N* silver nitrate (a total of 20 ml. is usually sufficient for samples of phosphate rock), heat on the steam bath for 0.5 hour, stirring occasionally, cool to room temperature in a dark place, and then filter and wash with cold water. Add 5 ml. of ferric alum solution to the filtrate and determine the excess silver by titration with 0.1 *N* potassium thiocyanate. Subtract the amount of silver found in the filtrate from that originally added. The difference represents the silver required to combine with the chlorine in the lead chlorofluoride and from this the fluorine content is calculated, 1 ml. of 0.1 *N* silver nitrate being equivalent to 0.00190 gram of fluorine.

[6] If large quantities of lead sulfate are present the precipitate dissolves slowly, but this does not affect the results.

Results Obtained by Fusion–Acid Extraction and Volatilization Methods on Various Phosphatic Materials

Table IV gives a comparison of results for fluorine in various phosphatic materials as determined by the fusion–acid extraction and the volatilization methods. With the exception of one sample, No. 930, oxidizing agents were not used in the fusion mixtures. In all cases the figures actually determined are given, no corrections being made for failure of the methods to give complete recovery of the fluorine.

Table IV—Comparison of Recovery of Fluorine by Combined Fusion and Acid Extraction Method and by Volatilization Method

Sample	Material[a]	Fluorine Recovered by: Fusion and acid extraction method	Volatilization method
		Mg.	*Mg.*
...	$Ca_3(PO_4)_2$, 0.7 g. + CaF_2, 0.0821 g.[b]	36.9	35.4
...	Tennessee brown-rock phosphate[c]	33.3	33.3
912	Florida pebble phosphate, high grade	36.8	36.2
947	Florida pebble phosphate, low grade	36.4	37.5
932	Florida hard-rock phosphate	36.8	36.4
726	Florida waste-pond phosphate	20.1	16.9
727	Florida waste-pond phosphate	19.4	13.5
930	Tennessee blue-rock phosphate	32.0	35.3
930	Tennessee blue-rock phosphate	33.9[d]	35.3
448	Tennessee blue-rock phosphate	32.5	34.3
449	Tennessee blue-rock phosphate	36.1	36.9
983	Electric phosphoric acid furnace slag	35.7	11.6
1005	Electric phosphoric acid furnace slag	35.1	15.0
1006	Electric phosphoric acid furnace slag	35.7	18.7
999	Experimental phosphoric acid blast furnace slag	6.9	1.1
1141	Fluorspar basic slag	11.9	9.4
1142	Fluorspar basic slag	10.9	9.2

[a] One-gram samples of all materials except $Ca_3(PO_4)_2$–CaF_2 mixture.
[b] Contained 37.9 mg. of fluorine.
[c] Bureau of Standards standard sample No. 56. Contained approximately 34.5 mg. of fluorine.
[d] 0.1 gram KNO_3 added to fusion mixture.

Although it seems quite certain that neither method, as developed at present, gives complete recovery of the fluorine in phosphate rock, they both give about the same results on commercial grades of Tennessee brown-rock, Florida pebble, and Florida hard-rock phosphate, while the fusion–acid extraction method gives decidedly lower results than the volatilization method on Tennessee blue-rock phosphate. The volatilization method is, therefore, recommended for the analysis of the usual commercial grades and types of phosphate rock. On the other hand, the fusion–acid extraction method gives much higher results than the volatilization method on Florida waste-pond phosphates (*5*) and slags, which contain considerable quantities of silicates, and is recommended for the analysis of these and similar materials.

Literature Cited

(1) Daniel, *Z. anorg. Chem.*, **38**, 299 (1904).
(2) Ditte, *Compt. rend.*, **94**, 1592 (1882).
(3) Fairchild, *J. Washington Acad. Sci.*, **20**, 141 (1930).
(4) Hawley, Ind. Eng. Chem., **18**, 573 (1926).
(5) Hill, Jacob, Alexander, and Marshall, *Ibid.*, **22**, 1392 (1930).
(6) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 805, Wiley, 1929.
(7) Hoffman and Lundell, *Bur. Standards J. Research*, **3**, 581 (1929).
(8) Marvin and Schumb, *J. Am. Chem. Soc.*, **52**, 574 (1930).
(9) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, p. 897, Longmans, 1923.
(10) Muehlberg, Ind. Eng. Chem., **17**, 690 (1925).
(11) Reynolds, Jacob, and Hill, *Ibid.*, **21**, 1253 (1929).
(12) Reynolds, Ross, and Jacob, *J. Assocn. Official Agr. Chem.*, **11**, 225 (1928).
(13) Rose, *Pogg. Ann.*, **77**, 292 (1849).
(14) Starck, *Z. anorg. Chem.*, **70**, 173 (1911).
(15) Treadwell and Hall, "Analytical Chemistry," Vol. I, p. 408, Wiley, 1916.
(16) Wagner and Ross, J. Ind. Eng. Chem., **9**, 1116 (1917).

Effect of Certain Forms of Silica on Determination of Fluorine by Volatilization Method[1]

D. S. Reynolds and K. D. Jacob

FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

Silica gel which has not been ignited at temperatures above 1000° C., and silicates which are decomposable by sulfuric acid, may have a very deleterious effect on the determination of fluorine by the volatilization method. This seems to be owing to the formation of a nonvolatile silicon oxyfluoride, probably $SiOF_2$. Silica gel which has been ignited at 1100° C. or higher temperatures is as effective as quartz as a source of silica for the determination.

The volatilization method does not give reliable results for fluorine in slags and certain natural phosphates containing acid-decomposable silicates.

As POINTED out in a preceding paper (*9*), the volatilization method for the determination of fluorine may give very low results in the presence of certain forms of silica. This fact was stressed in 1904 by Daniel (*2*) who observed that less than 10 per cent of the total fluorine was volatilized as silicon tetrafluoride when mixtures of 0.1031 to 0.1092 gram of pure calcium fluoride and 2 grams of precipitated silicic acid were treated with concentrated sulfuric acid. He also observed that decreasing the weight of precipitated silicic acid resulted in somewhat better recoveries of fluorine. Similar results were obtained by Casares (*1*) on mixtures of calcium fluoride and silica gel, or calcined sodium silicate. The results of some experiments carried out by Daniel indicate that the poor recoveries of fluorine in the presence of silicic acid are due at least in part to the formation of a nonvolatile silicon oxyfluoride, probably $SiOF_2$.

Daniel obtained excellent results on pure calcium fluoride when powdered quartz was used as the only source of silica, and Casares obtained good results by the use of powdered glass. (Casares used degelatinized photographic plates which have approximately the same composition as ordinary window glass.) Although powdered quartz is generally used as the source of silica in the determination of fluorine by the volatilization method, the effect of other forms of silica is of particular importance since they may occur in fluorine-bearing materials. The present paper gives the results of a brief investigation of this subject, with particular reference to the determination of fluorine in highly siliceous phosphatic materials.

Effect of Form of Silica

The volatilization method for fluorine as outlined by Wagner and Ross (*12*) and modified by Reynolds, Ross, and Jacob (*4, 11*)[2] was used in this study. Unless stated otherwise, commercial quartz flour that had been ignited at 900° to 1000° C. was used. All the silica-bearing materials were ground to 200 mesh. The fluorine-bearing materials were ground to pass a 100-mesh sieve, and in some cases a 200-mesh sieve.

In the first series of experiments, the recovery of fluorine from fluorspar of known fluorine content in the presence of quartz, glass, and silica gel, as respective sources of silica, was determined. The crystal quartz was originally in the form of large colorless crystals which were heated to about 900° C. and plunged into cold water in order to facilitate grinding them to a fine powder. The silica gel was a commercial activated material.

The results given in Table I show that approximately the same recoveries of fluorine were obtained when either commercial quartz flour, crystal quartz, or glass photographic plate were used as sources of silica. The recoveries ranged from 92.6 to 95.9 per cent of the total fluorine present, which is in good agreement with results previously obtained (*11*). It has been pointed out (*11*) that boron compounds have a deleterious effect on the determination of fluorine by the volatilization method. The low recoveries in the presence of powdered Pyrex glass were probably due to the boron content of the glass.

Table I—Effect of Form of Silica on Determination of Fluorine by Volatilization Method

(0.05 gram of fluorspar plus 1 gram of 200-mesh siliceous material)

Form of Silica	Fluorine Present	Fluorine Recovered	
	Mg.	*Mg.*	%
Commercial quartz flour, unignited	23.1	21.4	92.6
		21.5	93.1
Commercial quartz flour, ignited for 1 hour at 950° C.	23.1	21.5	93.1
		21.9	94.8
Crystal quartz, unignited	23.1	21.4	92.6
		21.5	93.1
Crystal quartz, ignited for 1 hour at 950° C.	23.1	21.6	93.5
		21.8	94.4
	24.2[a]	22.8	94.2
		23.2	95.9
Glass, photographic plate	23.1	21.4	92.6
		21.6	93.5
		21.7	93.9
Glass, Pyrex[b]	23.1	19.5	84.4
		21.1	91.3
Silica gel[c]	23.1	2.0	8.7
		5.6	24.2
Silica gel, ignited 1 hour at 900° to 1000° C.	23.1	17.2	74.5
		19.3	83.5
Silica gel, ignited 3 hours at 1000° C.[d]	23.1	17.9	77.5
		20.2	87.4
Silica gel, ignited 0.5 hour at 1100° C.	23.1	21.4	92.6
		22.0	95.2
Silica gel, ignited 0.5 hour at 1150° C.[e]	23.1	21.5	93.1
		21.5	93.1

[a] Fluorspar crystals containing 99.6 per cent CaF_2 used. Bureau of Standards fluorspar 79 used in other experiments.
[b] Contained 12 per cent B_2O_3.
[c] Commercial activated gel.
[d] Ignition loss, 11.58 per cent.
[e] Ignition loss, 11.71 per cent.

In the presence of commercial activated silica gel, only 9 to 24 per cent of the total fluorine was recovered. Apparently, the low recovery was not due merely to the presence of moisture in the gel, since this material lost only 11.71 per cent of its weight upon heating for a half hour at 1150° C. Furthermore, it has been shown (*11*) that almost as good recovery of fluorine in pure calcium fluoride is obtained by the use of 96 per cent sulfuric acid as by the use of 98 per cent acid. Consequently, the addition of as much as 1

[1] Received May 14, 1931.

[2] The features of the modified method include (1) the use of an improved form of flask for digesting the fluorine compound with silica and sulfuric acid; (2) the use of an electric furnace for heating the digestion flask, in order to obtain closer temperature control; (3) the removal of the silicon tetrafluoride from the digestion flask by means of moisture-free air under slightly reduced pressure; (4) the elimination of the use of anhydrous copper sulfate as a dehydrating agent in the digestion flask; and (5) the titration of the hydrofluosilicic acid in boiling hot solution.

gram of water to the 40 ml. of 98 per cent acid used in these determinations would not have affected the results to a significant extent. Much better recoveries of fluorine were obtained when the silica gel was ignited at high temperatures, but ignition at 1100° C. was necessary in order to obtain results comparable with those obtained by the use of ground quartz as a source of silica. The foam which characterizes the presence of fluorine when quartz is used as the source of silica does not form on the surface of the sulfuric acid when ordinary silica gel is used. It forms, however, when the gel is ignited at 1000° C., or higher temperatures.

The chemical nature of silica gel is a controversial question, but the results obtained in this investigation indicate that at least a portion of the silica is present in the form of silicic acids, and that progressively larger quantities of anhydrous silica are formed as the ignition temperature is increased. The work of Miehr, Koch, and Kratzert (*7*) indicates that ignition at a temperature of approximately 1200° C. is necessary to completely dehydrate precipitated silica. Patrick, Fraser, and Rush (*8*) have shown that adsorption by silica gel drops to a minimum in the case of gels heated for 2 hours at 1000° C., and that upon prolonged heating at 1100° C. the pure gel acquires a crystalline structure.

The second series of experiments related to the effect of various amounts of different silicates on the recovery of fluorine from mixtures of 0.05 gram of fluorspar and 1 gram of commercial quartz flour. The silicates were thoroughly mixed with the quartz flour and fluorspar. The samples of synthetic calcium silicates were kindly furnished by R. H. Bogue of the National Bureau of Standards. They were prepared by heating lime and silica to high temperatures. The iron blast furnace slag contained a small quantity of fluorine, and the results given in Table II have been corrected accordingly. The silica gel was a commercial activated material and was used without further heating.

Table II—Effect of Silicates on Recovery of Fluorine in Presence of Quartz Flour

(0.05 gram of fluorspar, Bureau of Standards sample 79, plus 1.0 gram of commercial quartz flour)

Silicate Added		Fluorine Recovered[a]	
Form	Weight		
	Gram	*Mg.*	*%*
None	0.0	21.9	94.8
		21.5	93.1
$3CaO.SiO_2$, synthetic	0.4	13.9	60.2
		15.5	67.1
	0.2	18.7	81.0
		20.8	90.0
	0.1	21.3	92.2
		21.5	93.1
β $2CaO.SiO_2$, synthetic	0.4	15.1	65.4
		18.9	81.8
	0.2	19.7	85.3
		19.9	86.1
	0.1	21.0	90.9
		22.2	96.1
γ $2CaO.SiO_2$, synthetic	0.4	14.1	61.0
		15.2	65.8
	0.2	19.5	84.4
		18.6	80.5
	0.1	21.8	94.4
		21.2	91.8
Iron blast furnace slag	0.5	14.1	61.0
		17.9	77.5
Silica gel[b]	0.5	11.9	51.5
		11.6	50.2

[a] 0.05 gram of fluorspar contained 23.1 mg. of fluorine.
[b] Commercial activated gel.

The results given in Table II show that the recovery of fluorine was reduced to a very considerable extent by the presence of 0.4 to 0.5 gram of calcium silicate, slag, or silica gel. Higher recoveries were obtained when the quantity of silicate was decreased, the average recovery in the presence of 0.1 gram of silicate being nearly as high as that obtained with quartz alone. The low results in the presence of the silicates may be explained by the formation of silicon oxyfluoride as a result of the action of hydrofluoric acid on the silicic acid formed by the reaction of sulfuric acid with the silicate. Silicates, such as glass, which are not decomposed by sulfuric acid would not, therefore, be expected to form the oxyfluoride.

Recovery of Fluorine in Highly Siliceous Phosphatic Materials

The commercial grades of phosphate rock produced in the United States usually contain less than 10 per cent of total silica (SiO_2), which is present principally in the form of quartz. The fluorine content of such materials (*6*, *10*) can be determined about as accurately as that of pure calcium fluoride by means of the volatilization method. Certain types of natural phosphates—for example, the soft and waste-pond phosphates of Florida (*3*, *5*)—contain, however, 10 to 30 per cent of total silica. This silica is usually present in a very finely divided condition, and in many samples a considerable portion of it is no doubt combined in the form of silicates. The fluorine in the natural phosphates is present principally as complex fluorphosphates and perhaps also to a small extent as calcium fluoride.

Table III—Fluorine Content of Highly Siliceous Phosphatic Materials as Determined by Volatilization and Fusion–Acid Extraction Methods

Sample	Material	Fluorine Content[a] By volatilization[b]	By fusion–acid extraction[c]
		%	%
726	Florida waste-pond phosphate, 19.78% total SiO_2	1.69	2.01
934	Colloidal material from 726, 26.20% total SiO_2	0.76	1.56
727	Florida waste-pond phosphate, 23.27% total SiO_2	1.35	1.88
915	Florida waste-pond phosphate, 16.80 per cent total SiO_2	1.32	1.79
1091	Florida soft phosphate, 21.46% total SiO_2	1.74	2.17
983	Slag from commercial phosphoric acid electric furnace	1.16	3.57
1005	Slag from commercial phosphoric acid electric furnace	1.50	3.51
1006	Slag from commercial phosphoric acid electric furnace	1.87	3.57
999	Slag from experimental phosphoric acid blast furnace	0.11	0.69
1190	Slag from commercial phosphoric acid blast furnace	0.20	1.78
1191	Slag from commercial phosphoric acid blast furnace	0.18	2.00
1141	Fluorspar basic slag	0.94	1.19
1142	Fluorspar basic slag	0.92	1.09

[a] Actually determined figures, no correction being applied for failure of methods to give complete recovery of fluorine.
[b] 1-gram samples plus 1 gram of commercial quartz flour.
[c] 1-gram samples fused with 2 grams of sodium carbonate and 0.5 gram of silica.

The results given in Table III show that the figures for fluorine in several samples of highly siliceous natural phosphates as determined by the volatilization method were much lower than those obtained by the fusion–acid extraction method outlined in a preceding paper (*9*). The low results obtained by the volatilization method were not due to failure of the sulfuric acid to effect complete decomposition of the fluorine compounds originally present, but were, no doubt, due to the formation of a nonvolatile silica-fluorine compound.

The results (Table III) show that the volatilization method gives very low values for fluorine in slags such as those obtained in the manufacture of phosphoric acid by furnace processes. This may be owing to the presence of fluorine compounds which are not decomposed by sulfuric acid. However, these slags consist largely of silicates which are decomposed by sulfuric acid, and even if the original fluorine compounds were converted completely into hydrofluoric acid, a considerable portion of the latter would react with the silicic acid to form silicon oxyfluoride.

It is evident that the volatilization method for fluorine as used at present may give very unreliable results in the presence of precipitated silica and of silicates that are decomposed by sulfuric acid.

Literature Cited

(1) Casares, *Ann. soc. españ. fís. quím. (tec.)*, **27**, 290 (1929).
(2) Daniel, *Z. anorg. Chem.*, **38**, 290 (1904).
(3) Hill, Jacob, Alexander, and Marshall, Ind. Eng. Chem., **22**, 1392 (1930).
(4) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 600, Wiley, 1929.
(5) Jacob, Hill, and Holmes, Colloid Symposium Annual, Vol. VII, p. 195 (1930).
(6) Jacob and Reynolds, *J. Assocn. Official Agr. Chem.*, **11**, 237 (1928).
(7) Miehr, Koch, and Kratzert, *Z. angew. Chem.*, **43**, 250 (1930).
(8) Patrick, Fraser, and Rush, *J. Phys. Chem.*, **31**, 1511 (1927).
(9) Reynolds and Jacob, Ind. Eng. Chem., Anal. Ed., **3**, 366 (1931).
(10) Reynolds, Jacob, and Hill, Ind. Eng. Chem., **21**, 1253 (1929).
(11) Reynolds, Ross, and Jacob, *J. Assocn. Official Agr. Chem.*, **11**, 225 (1928).
(12) Wagner and Ross, J. Ind. Eng. Chem., **9**, 1116 (1917).

Stillhead for Laboratory Columns[1,2]

E. B. Kester and R. Andrews

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

THE most satisfactory type of stillhead for column fractionation in the laboratory is one simple in construction, attachable to the column without rubber or cork connections, suitable for both low- and high-boiling liquids, and designed to minimize hold-up. Also, it should permit the operator to establish a reflux ratio commensurate with the sharpness of fractionation desired. Column elongation should not produce severe mechanical strains.

The stillhead shown in Figure 1 made of Pyrex glass, combines most of these qualities. For attaching to the column, it is provided with a standard interchangeable ground-glass joint 25 mm. in diameter at the end. Immediately above is attached a drip point for the purpose of throwing the descending condensate to the center of the column so that it may distribute itself over the packing. Otherwise, the liquid would merely run down the sides and come in contact with very little of the ascending vapor.

The heavy part of the stillhead—that is, the condenser—is, when installed, in line with the column itself. This arrangement is almost a necessity in a long glass assembly of this kind where a rigid type of connection is employed, because of the upward expansion that is likely to occur. In the present instance, such expansion merely lifts the stillhead with it and produces no beam action whatever. The only horizontal appendage carried is a light side arm which can be supported by a brace integral with that used for the condenser.

Other details of construction and operation of this stillhead can best be understood by referring to the diagram. The ascending vapors rise through port *A* and on up through ports *B* into the reflux condenser. The liquid formed runs down through drip point *C* and into the off-take as far as cock *D*, which is kept closed until equilibrium has been established. An overflow of condensate through *E* is very quickly produced, which proceeds into the column by way of drip point *J*.

When the low-boiling constituent has concentrated in the head, as indicated by the thermometer at the top of the column reaching a minimum, valve *D* can be cracked to a point where the desired drop ratio exists between *C* and *G*.

H is a cooling device to prevent loss through evaporation by reducing the temperature of the liquids that pass through *D*. It need only be about 6 inches (15.24 cm.) long and of slim construction to avoid bulkiness and undue weight. Incidentally, its jacket may be in series with the condenser jacket.

Cock *D* is best equipped with a hollow key if high-boiling liquids are to be fractionated, as the possibility of its breaking from heat strains in contrast with the ordinary solid key is very little. Slots filed on either side of the aperture at both ends are of assistance in adjusting the reflux ratio properly.

Capillary tubing of 2-mm. bore should be used in the off-take as far as *D* to minimize hold-up, but between *D* and *G* standard tubing is satisfactory.

Once installed and the clamps adjusted to eliminate strains completely, a stillhead of this type can be used to good advantage in the fractionation of corrosive or non-corrosive liquids boiling over wide temperature ranges. One in operation in this laboratory for the fractionation of tar distillates and high-boiling tar acids is proving quite satisfactory. The standard ground-glass joint is an ideal type of connection and can also be successfully used for attaching flasks to the base of the column. Where phenols have to be distilled, for example, it is of great value, as cork and rubber are eaten away very quickly with the result that the distillate becomes contaminated.

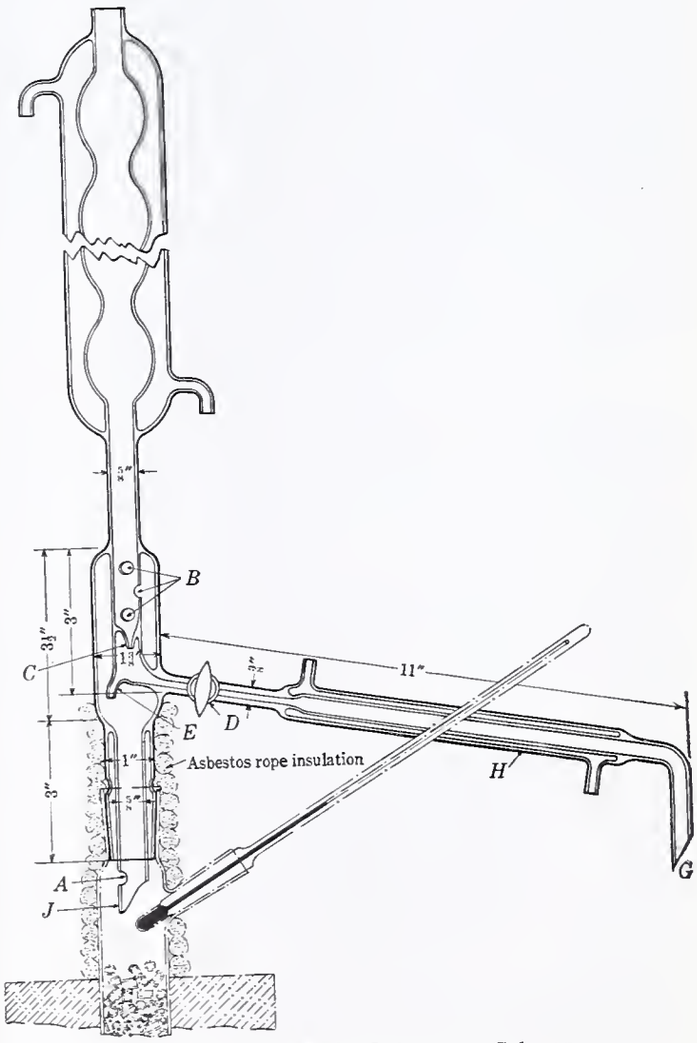


Figure 1—Stillhead for Laboratory Column

[1] Received May 19, 1931.
[2] Published by permission of the Director, U. S. Bureau of Mines.

(Not subject to copyright.)

The pH of Butter and Its Relation to Titratable Acidity[1]

B. H. Nissen

Research Laboratory, Blue Valley Creamery Co., Chicago, Ill.

A method is outlined for the titratable acidity of butter, and another for the hydrogen-ion concentration of butter. Various factors affecting these methods are discussed and certain peculiarities observed. A chart of values and a table showing the relationship of pH to titratable acidity of a large number of various lots of butter is given. The hydrogen-ion concentration is believed to be somewhat more reliable as a method for the reaction of butter.

IN STUDYING the chemistry of churning and the production of butter of fine flavor and good keeping quality, it is desirable to have at hand reliable methods for the acidity of not only the cream and buttermilk, but also that of the butter itself. Ordinary titration serves quite adequately for cream and buttermilk, but when applied to butter the results are not so definite. The acidity titration of butter has been investigated by Hunziker, Cordes, and Nissen (*4*) as a preliminary study to the entire problem of the keeping quality of butter and its relation to hydrogen-ion concentration. In this work the pH of butter and its titratable acidity have been studied.

In his report on butter to the Official Agricultural Chemists, Hortvet (*2*) in 1926 stated that a method for determining the acidity of butter would be of considerable value to dairymen and suggested "that a test designed for this purpose be investigated and if possible included in the official methods." No such test, even of tentative form, appears to have been offered by the above committee to date, and the literature as a whole contains relatively little on the subject.

Several investigators refer to the acidity of butter fat and of butter as determined by titration in alcohol-ether solution. Thus Sherman (*8*) states that such a value may be considered a measure of the rancidity of the fat, and Haglund and Waller (*1*) in a similar way employ such acidity figures in their studies of keeping quality. Only one reference was found to the use of water only as the diluent for the butter. This was a method described by Spitzer (*5*) in which no fat solvent at all was employed, the butter when melted in warm water being titrated directly with standard alkali.

Method for Titratable Acidity of Butter

After studying the various methods which appeared applicable for the determination of butter acidity, it was decided that the use of warm water mixtures in reality gave results which are most desirable for general application to the study of keeping quality. The method adopted consists of titrating an 18-gram sample of the butter in 90 cc. of previously boiled and partially cooled distilled water at about 60° C. with 1 cc. of phenolphthalein as indicator. There is considerable fading of the end point in the earlier part of the titration. Accordingly, a time limit was established for the titration. The greater part of the standard alkali required by a particular sample is added quite rapidly in the first part of the test until a fairly permanent pink color is obtained. This usually requires less than about one-half minute. The addition of alkali and the agitation is, however, continued until 3 minutes have been consumed in all. Only enough additional alkali is added during the final stirring to maintain the color of the test mixture fairly uniform. A light but definite pink color should then be evident in the aqueous layer when the fat rises on discontinuing the agitation. There may be some justification in stopping the titration at the first permanent coloration as is done in most ordinary titrations, but in the case of butter the end point is so uncertain, especially in the earlier stages of the titration, as to make comparable results rather difficult. The additional period provided permits a better adjustment of the color selected for the end point and is of sufficient duration to be applicable to even the most acid butter samples usually encountered.

Fading of the end point is much more pronounced in methods using alcohol and alcohol-ether mixtures, and would seem to be a serious disadvantage to their use. Furthermore, the end point color obtained does not remain long enough after the titration is completed, even when carried for a 10-minute titration period, to make final comparisons with a standard color possible, as can be done in the aqueous method.

In addition, titration values with these solvents give results which are considerably greater than those for aqueous mixtures. From two to three times as much standard alkali is absorbed by the butter when it is suspended in alcohol or alcohol-ether as when in water alone. This is shown in Table I where, for matter of comparison, the number of cubic centimeters of 0.02 *N* standard alkali required in each case by an 18-gram sample of butter is reported.

Table I—Comparison of Titration of Butter in Aqueous Mixture with That in Alcoholic and Alcohol-Ether Mixtures

Lot	Aqueous Mixture	Alcohol-Ether Mixture	Alcoholic Mixture
	Cc.	*Cc.*	*Cc.*
1	10.3	22.0	21.3
2	6.8	14.0	14.0
3	6.6	13.5	14.5
4	6.8	14.5	14.5
5	7.4	15.2	15.0
6	7.3	15.7	15.0
7	6.1	14.5	12.5
8	7.4	15.0	14.5
9	14.0	27.5	24.0
10	17.6	31.0	25.3
11	3.7	12.0	10.0
12	4.2	12.0	
13	4.0	11.0	
14	4.5	11.7	
15	4.5	10.5	
16	6.0	12.5	
17	3.8	9.5	
18	4.3	9.5	
19	4.0	12.2	
20	4.2	12.2	
21	7.8	17.5	
Av.	6.7	14.9	
Av. of first 11 values	8.5	17.7	16.4

No definite relationship appears to exist between the values for the three types of solvents except that where the water titration is low, that of the others is low too. Obviously it would not be fair to consider this acidity as solely lactic, since the acids of the fat are also included. Such results are sometimes termed "acid number" and expressed as the number of milligrams of alkali absorbed by 1 gram of fat or oil.

It would seem that these two types of values—i. e., the acidity as obtained in an alcohol-ether mixture and that in an aqueous mixture—really serve distinct and separate purposes. The first may be considered in general a measure of the

[1] Received April 18, 1931. Presented before the Division of Agricultural and Food Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

rancidity of the fat and the effects of fat splitting or oxidative processes, while the second reflects approximately merely the degree of titratable acidity of the cream at churning time. In studies of cream neutralization and in any churning experiments where titratable acidity of the cream is a factor of prime consideration, it would seem that the titration of the butter in an aqueous medium is the only correct procedure to follow. In such cases it is really only the serum acid we are interested in, both in the cream as well as in the butter.

The titration of butter differs from that of other dairy products in the marked fading of the end point color, as mentioned above. The absorption of alkali diminishes gradually as the titration proceeds, and may even become constant during the last 3 or 4 minutes. It is probable that the fading of the end point may be due to an absorption of the alkali by some constituent either of the fat or of the curd portion. Peculiarly, neither the fat alone nor the curd portion exhibits this fading end point to the same degree. Table II shows this absorption of alkali as the titration is continued.

Table II—Absorption of Alkali during Titration of Butter with Standard Alkali

(Cc. of 0.02 *N* sodium hydroxide required by 18-gram sample of butter in 90 cc. of warm water with continuous agitation during titration—i. e., for 10 minutes)

Sample	Duration of Titration in Minutes									
	1	2	3	4	5	6	7	8	9	10
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
1	4.2	5.0	5.5	5.7	5.9	6.0	6.0	6.0	6.0	6.0
	4.2	5.0	5.5	5.5	5.7	6.0	6.0	6.0	6.0	6.1
2	2.5	3.0	3.5	3.7	4.0	4.5	4.7	5.0	5.0	5.0
	2.5	3.0	3.5	3.7	4.0	4.5	4.7	4.8	4.8	4.8
3	1.5	2.0	2.2	2.5	2.6	2.7	2.7	2.7	2.7	2.7
	1.5	2.0	2.0	2.2	2.5	2.6	2.7	2.7	2.7	2.7
4	5.3	7.0	7.9	8.3	8.7	9.0	9.3	9.5	9.6	9.6
	6.2	7.6	8.2	8.6	8.9	9.1	9.3	9.5	9.7	9.7
5	5.4	6.7	7.7	8.4	8.9	9.3	9.6	9.9	10.1	10.1
	5.2	6.9	8.0	8.6	9.0	9.4	9.7	10.0	10.2	10.2
6	5.4	6.5	7.1	7.8	8.0	8.2	8.5	8.7	8.9	9.0
	5.5	7.2	7.7	8.5	8.8	9.0	9.2	9.1	9.2	9.2
7	3.0	4.0	4.2	4.5	4.5	4.7	5.0	5.0	5.0	5.0
	2.5	3.5	3.7	4.2	4.5	4.6	4.7	4.8	4.9	5.0
8	2.0	2.2	2.5	2.7	3.0	3.5	4.0	4.2	4.2	4.2
	2.7	2.7	2.7	3.0	3.5	3.7	4.0	4.2	4.2	4.2
9	7.5	8.5	8.7	9.0	9.0	9.2	9.4	9.5	9.6	9.7
	7.2	8.0	8.5	8.7	9.0	9.0	9.2	9.2	9.4	9.5
Curd-serum water mixture of No. 9	3.5	3.5	3.5	3.5	3.5	3.7	3.7	3.7	3.7	3.7
Fat-curd water mixture of No. 9	2.5	2.5	2.7	3.0	3.5	3.5	3.7	3.7	3.7	3.7
Fat only in water of No. 9	0.7	0.8	1.0	1.2	1.2	1.2	1.5	1.5	1.5	1.5
Butter in alcohol-ether from No. 9	17.0	18.0	19.0	19.2	19.5	19.7	20.0	20.5	20.5	20.5
Butter in alcohol-ether:										
Sample I	13.0	14.2	15.0	15.5	15.6	15.7	16.0	16.2	16.5	16.8
Sample II	10.5	11.0	11.5	12.0	12.4	12.8	12.8	13.0	13.2	13.2

Just what point should be chosen as the correct end point of the titration or whether any of these values justify a designation as butter acidity is, of course, a matter of conjecture. It is enough to say, however, that the values for the 3-minute titration of butter do, in general, reflect the titratable acidity of the cream at churning time. Ordinarily, cream of an acidity of about 0.15 per cent gives butter of an acidity of 0.02 to 0.04 per cent; cream of 0.25 per cent acidity gives butter of 0.03 to 0.05 per cent; cream of 0.3 per cent acid gives butter of 0.05 to 0.07 per cent; cream of 0.5 per cent acid produces butter having an acidity around 0.10 to 0.12 per cent; whereas real acid cream, around 0.8 per cent, produces butter with an acidity as expressed by the 3-minute titration of about 0.17 to 0.20 per cent. However, this cannot be considered a rigid scale of comparison, for certain inexplicable factors cause numerous variations outside of the ranges given in the above. Information on the relation between the acidities of cream and that of butter, as well as the important factors influencing this relationship and its effect on the keeping quality of butter, are given by Hunziker (*3*).

Because of the small acidities present in the butter, it was thought that the carbon dioxide of the air may be an interfering factor. Considerable experimentation in this connection, such as titration under vacuum and in presence of carbon dioxide–free air, showed the effect of carbon dioxide to be negligible.

Attempts were made to perform this titration by electrometric means using both the hydrogen electrode as well as the quinhydrone procedure. Peculiarly, however, the pH of the pink aqueous mixture resulting after the titration of a sample of butter in the usual way was always considerably lower than that usually accepted as the true end point for phenolphthalein—i. e., around 8.2 to 8.4. Yet the aqueous layer remained definitely pink. Other dairy products titrated to a similar pink end point, however, showed about normal hydrogen-ion values, as is shown in Table III.

Table III—Hydrogen-Ion Concentration of Butter-Water Mixtures and Other Dairy Products after Titration to Usual Pink Phenolphthalein End Point

Mixture	Treatment of Sample	Sample	pH of Sample Titrated to Pink Phenolphthalein End Point
A	Butter titrated in usual way; water-serum portion after fat had risen which required only few minutes; this liquid definitely pink	1	7.51
		2	7.33
		3	7.64
		4	7.63
		5	7.54
		6	7.42
		7	7.73
		8	7.39
B	Buttermilk plus equal volume of water titrated to usual pink phenolphthalein end point	1	8.20
		2	8.33
		3	8.23
		4	8.27
C	Cream plus equal volume of water titrated to usual phenolphthalein end point	1	8.42
		2	8.38
		3	8.39
		4	8.45
		5	8.35
D	Whole milk plus equal volume of water titrated to usual phenolphthalein end point	1	8.45
		2	8.52
		3	8.46

Even in the case of butter samples definitely over-titrated, the pH of the aqueous portion was always well below 8.0. Just what could be the cause of this phenomenon was difficult to explain, except that perhaps an error of some kind had been introduced due possibly to high dilution, high sodium chloride content (for salted butter), or the release of salts absorbed by the proteins in sufficient quantity during the titration to lower the normal end point of phenolphthalein.

Method for Determining pH of Butter

As a further study of the reaction involved in the churning of cream, methods for the determination of true acidity were also applied to the various products involved. Considerable difficulty was experienced, however, and no references could be found in the literature to the pH of butter at the beginning of this work. Butter was peculiar in itself and evidently unlike any other product of which both electrometric and colorimetric technic for hydrogen-ion determinations is dealt with in the literature.

On account of the lack of electrical conductivity, the whole butter itself cannot be used as such in the determination of pH. Absolutely no current flow is registered when the hydrogen and calomel electrodes are properly arranged in a soft paste of the butter, nor even when the quinhydrone electrode is used as recommended by Watson (*10*) for cheese. On the other hand, excellent results are secured with other products, and even with the recently introduced plastic cream of a richness between 75 and 80 per cent fat and physically resembling butter.

The following procedure for the pH of butter was finally adopted: About one pound (0.45 kg.) of butter was melted in a sealed Mason jar at a temperature of about 160° to 170° F. (71.11° to 76.67° C.). Approximately 1 hour of heating is necessary to secure complete melting and a separation of the fat. The curd-serum layer is removed by means of a pipet as completely as possible from beneath the fat layer, and well mixed. Hydrogen-ion values are obtained directly on this

separated curd-serum mixture by either the Clark shaking electrode or the Hildebrand electrode, the Leeds and Northrup type K potentiometer equipment being used as the voltage-recording apparatus. To facilitate accurate control of temperature, the beaker containing the electrodes is immersed in a thermostatically controlled water bath and the whole apparatus mounted in a cabinet whose temperature is also under control.

The quinhydrone procedure using a saturated calomel cell and the gold spiral electrode gave results comparing very well with those obtained by the hydrogen electrode and was accordingly adopted for the hydrogen-ion work on butter on account of its greater rapidity, equilibrium being established in usually less than 5 minutes.

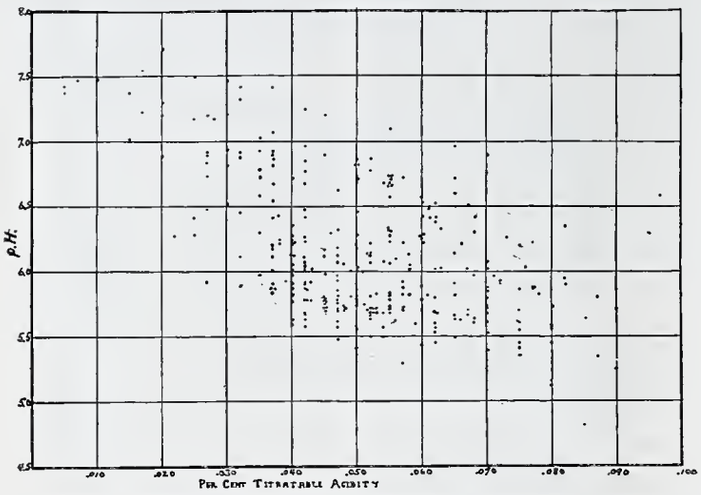


Figure 1—The pH of Butter as Related to Titratable Acidity

Whether or not hydrogen-ion determinations thus made on the curd-serum mixture of butter actually represent the true reaction of whole butter is as yet a matter for further study. Certain preliminary experiments, however, made in the author's own laboratory seem to justify the opinion that the fat has absolutely no effect on the pH of butter and acts merely as a diluent of the active substances present. Sharp and McInerney (*6*) hold a similar opinion in regard to cream.

In perfecting the above method for the pH of butter several factors which, because of the complex nature of the product involved, might justifiably be considered as possible sources of error have been carefully investigated by Hunziker, Cordes, and Nissen (*4*).

Relationship of pH and Titratable Acidity

Various investigators have reported comparisons between the hydrogen-ion concentration and the titratable acidity of fresh milk where the amount of free acid present is relatively small. One of these investigators (*9*) states that no exact relationship exists. Sharp and McInerney (*7*), on the other hand, show a relatively good agreement between titratable acidity and pH of sweet milk and an even better relationship for milk which has been allowed to sour.

A similar comparison of such values for butter—i. e., the titratable acidity and the hydrogen-ion concentration as determined by the modified procedures outlined above—are presented here. No attempt has been made to classify the butter as to source, treatment during manufacture, or composition of the main constituents. Such factors may all have a marked effect on the relationship to be expected and at times may cause one value to vary more than the other.

Figure 1, representing 325 samples of butter selected at random, shows merely a tendency towards such a relationship. In general, the majority of the titratable acidities for any particular hydrogen-ion concentration vary within less than ±0.015 per cent from a line drawn midway through the mass of individual values. In Table IV an attempt has been made to average the values in the graph, all of the acidities corresponding to an interval of 0.1 pH being grouped together. Two sets of averages are shown, those in the third column being an average of all the acidities in any particular group. These show several rather wide variations, however, and may not form as correct a picture as the values in the last column which were obtained from a median on the graph. These latter figures form a beautiful scale, but unfortunately are not always possible of realization experimentally. There must be many as yet unknown factors operating in this relationship between the hydrogen-ion concentration of butter and its titratable acidity which can only be clarified by a great deal of additional experimentation. Nevertheless, from a practical value it appears that the hydrogen-ion concentration forms a truer index of the real reaction involved in the churning operation and of the products formed.

Table IV—Relation of pH to Titratable Acidity of Butter
(Averages of values)

No. of Samples	pH Range	Butter Acidity: Av. of all values found	Butter Acidity: Av. value taken from graph
6	4.80–5.09	0.120	0.104
5	5.10–5.19	0.098	0.091
2	5.20–5.29	0.073	0.086
3	5.30–5.39	0.077	0.081
8	5.40–5.49	0.064	0.076
12	5.50–5.59	0.061	0.072
28	5.60–5.69	0.059	0.068
41	5.70–5.79	0.053	0.063
31	5.80–5.89	0.055	0.059
23	5.90–5.99	0.056	0.055
21	6.00–6.09	0.053	0.052
19	6.10–6.19	0.047	0.049
23	6.20–6.29	0.054	0.046
12	6.30–6.39	0.051	0.043
14	6.40–6.49	0.047	0 040
8	6.50–6.59	0.051	0.036
8	6.60–6.69	0.051	0.033
12	6.70–6.79	0.047	0.030
13	6.80–6.89	0 040	0.028
10	6.90–6.99	0.041	0.025
5	7.00–7.09	0.036	0.022
3	7.10–7.19	0.036	0.020
6	7.20–7.29	0.030	0.017
4	7.30–7.39	0.018	0.015
6	7.40–7.49	0 020	0.013
3	7.50–7.69	0.017	0.010

The methods presented for the titratable acidity and the hydrogen-ion concentration of butter, as well as the rather general relationship observed in the graph and Table IV, are presented with due consideration of the complex nature of the product involved. It is hoped, however, that these methods and data may encourage further investigation along similar phases of this rather important process, the manufacture of butter.

Literature Cited

(1) Haglund, E., and Waller, E., 1923 to 1929. *Medd. Centralanstalt. försöksväsendet jordbruks.*, Nos. 232, 261, 290, 321, 347 (1923–29).
(2) Hortvet, J., *J. Assocn. Official Agr. Chem.*, **9**, 231 (1926).
(3) Hunziker, O. F., "The Butter Industry," 2nd ed., 1927.
(4) Hunziker, O. F., Cordes, W. A., and Nissen, B. H., *J. Dairy Sci.*, **14**, 4 (1931).
(5) Hunziker, O. F., Spitzer, G., Mills, F. C., and Switzer, H. B., Purdue Agr. Coll., *Bull.* **208**, 45 (1917).
(6) Sharp, P. F., and McInerney, T. J., *J. Biol. Chem.*, **70**, 749 (1926).
(7) Sharp, P. F., and McInerney, T. J., *Ibid.*, **75**, 177 (1927).
(8) Sherman, H. C., "Methods of Organic Analysis," p. 147 (1917).
(9) Vandevalde, J. J., *Lait*, **7**, 140 (1927).
(10) Watson, F. D., *J. Dairy Sci.*, **12**, 289 (1929).

New Protein Conversion Factors—Investigations of proteins during recent years by the U. S. Department of Agriculture have resulted in the formulation of a new set of factors for converting the percentages of nitrogen in foods and feeds into protein equivalents. Comparisons for several foods show that the new conversion factors vary considerably from the single factor now in general use.

Data on the subject are presented in Department of Agriculture *Circular* **183-C**, copies of which may be obtained free from the Office of Information, U. S. Department of Agriculture, Washington, D. C.

Improved Gauze-Plate Laboratory Rectifying Column[1]

S. Palkin

Bureau of Chemistry and Soils, Washington, D. C.

An improved gauze-plate column is described which possesses the advantages of simplicity of construction and resistance to flooding, and has been found particularly well adapted for vacuum fractionation. Data in the form of graphs are given indicating the character of fractionation obtainable with this column.

Many attempts have been made to devise laboratory rectifying columns comparable to the bubbling-plate type frequently used in the industry. As a rule such columns for laboratory use require somewhat elaborate glassblowing. A device of this type which is simple in construction would doubtless find extensive use in laboratories. In this paper such a column, involving a minimum of glassblowing and structurally simple otherwise, is described.

An interesting evolution in the development of the bubbling column is evidenced in the literature, ranging from the earlier forms such as the Glinsky, Le Bel-Henninger, Brown, Young and Thomas (*6*, *7*), Taylor and Snyder (*3*), to the more recently improved bubbling cap-plate types described by Bruun (*1*). No attempt will be made in this paper to enter into any discussion of the relative merits and comparative effectiveness of bubbling columns (*1*, *3*) as against the packed form, evaporator, spiral (*5*), and others. This subject has been treated in standard works (*7*) and in numerous publications (*3*). The preferred type of fractionating device will depend to a large extent on the particular work for which it is to be used.

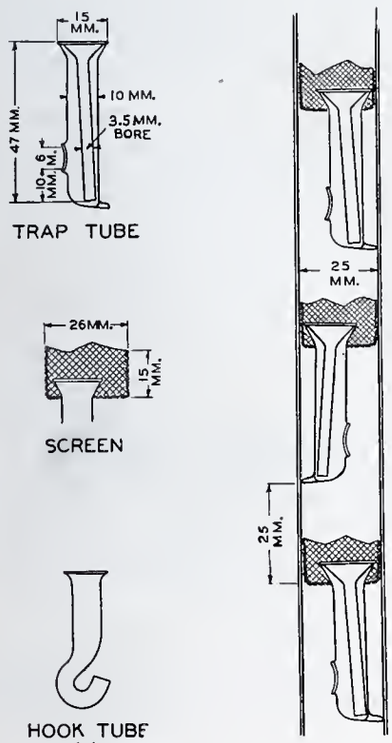


FIG. 1. COLUMN TUBE SHOWING STAGGERED POSITION OF TRAP TUBES.

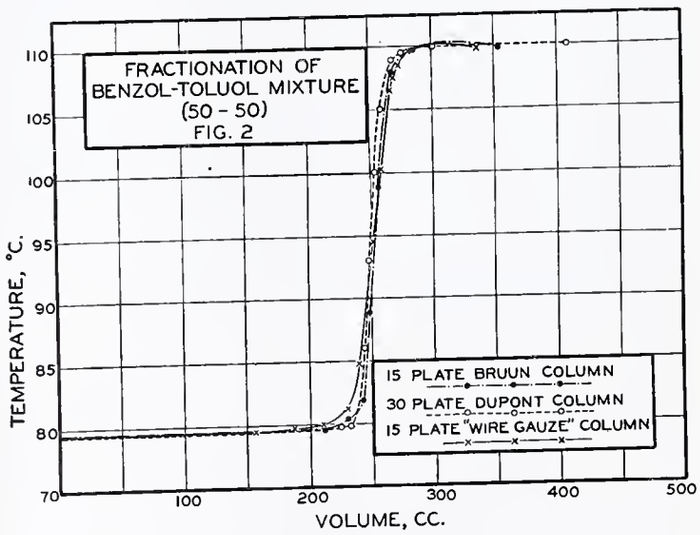
In this laboratory an efficient means for the fractional distillation in vacuum of a complex mixture such as turpentine was needed, one which, for high reflux ratio, is capable of handling comparatively large columns of vapor without undue tendency to flooding.

A structural feature essential for the efficient operation of bubbling columns in general is an adequate mechanism for the rapid transfer of reflux liquid down from plate to plate, in order to provide each with an appropriate scrubbing medium for the progressive enrichment of the ascending vapors in terms of the more volatile constituent.

Dupont (*2*) describes a two-meter plate column similar to that of Young and Thomas which he has found effective in the fractionation of turpentine. This device embodies simplicity of construction, since the internal mechanism consists only of a series of glass trap tubes hung in wire-gauze plates (inverted cup-shaped), the latter being held in the straight glass column tube by friction. The wire gauze automatically provides an effective means for producing intimate contact of descending liquid with ascending vapors.

Experience in this laboratory with the Dupont column has shown, however, that the trap tubes (Figure 1, *a*) do not function dependably. "Blowing" of vapors through these tubes with consequent flooding of compartments occurs, necessitating frequent interruption.

Careful observation has shown also that a portion of the reflux liquid in its course from trap tube to plate below finds its way directly into the opening of the next lower tube without forming a part of the pool of scrubbing medium of that plate, thus rendering the reflux partly ineffective.



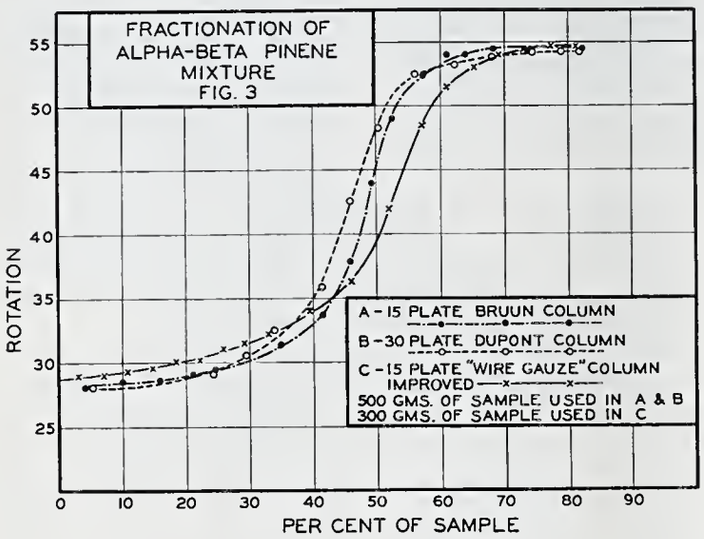
A Bruun column (*1*), fifteen-plate, available in this laboratory, although found to be a very effective fractionating device, also showed a tendency to flood when distilling in vacuum,[2] but much less so than the Dupont apparatus.

A simple modification of the Dupont and Young and Thomas columns through the use of an improved trap tube, shown in Figure 1, has been found to overcome completely the

[1] Received May 6, 1931. Presented before the Division of Agricultural and Food Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] An improved form of this column has recently been developed by the same author, Bureau of Standards, unpublished.

difficulties encountered in the former and to function with complete smoothness and dependability. Their straight test-tube form also permits a superimposed arrangement in staggered positions right and left rather than directly over each other, an arrangement not possible with the hook-form tube (Figure 1, *a*) of the Dupont apparatus. Since the integral parts, the wire-gauze plate and the glass trap tubes, can be easily made with ordinary laboratory facilities, construction of a long column is a relatively simple matter.



Construction of Apparatus

Trap Tubes—The simple glass manipulation involved in their construction may be expedited by proceeding in the following order: A small Pyrex test tube (stock size, 3 × $^3/_8$ inch, or 7.62 × 0.95 cm.) is used for the outer tube, and is made funnel-shaped at the top and a hole made at the point indicated. The inner tube, made funnel-shaped at the top and cut to length, is then simply fused in position, leaning, by rotating in the flame. The outer tube is then made to proper length by drawing off the lower end, leaving the tip at an angle as indicated. The volume of liquid in the reservoir portion of the trap tube, when primed, is calculated to provide sufficient head in the inner tube to insure against passage of vapors through it.

Wire-Gauze Plates—Nickel wire screen, 40-mesh, was found very serviceable in turpentine-oil fractionation. A form for pressing the screen into shape may be prepared by drilling a hole in a block of wood or metal, the diameter of the hole being about 1 or 2 mm. greater than the inside diameter of the column tube. The wire screen is cut into disks and pressed into the form with a metal plunger. The cup-shaped gauze plate is then trimmed to leave an even shoulder about 1 cm. high. A hole, the diameter of which is very slightly less than the outer diameter of the trap tube, is made with a round file. Distortions of the plate are eliminated by reshaping. The outer diameter of the gauze plates should be somewhat larger (1 to 2 mm.) than the inside diameter of the column tube, so that they may be held in position by friction.

Assembly of Column—The gauze plates, each with its trap tube, are inserted in the straight column tube in such a way that the trap tubes have the lower ends (the tips) touching the side of column tube and arranged in a staggered position as indicated in Figure 1. This will direct the flow of reflux liquid from each successive trap tube away from the top opening of the next lower trap tube. A long stick, provided with a metal or glass tube having an inside diameter sufficient to surround the trap tube loosely, has been found convenient for placing the units in position as illustrated.

Operation of Column—As a rule the trap tubes prime themselves after a few minutes of running the column "total reflux." This may also be expedited by allowing one or two of the spaces between the plates in the upper part of the column to flood and then effecting a return of the condensed liquid by varying the pressure when distilling in vacuum, by blowing into the apparatus for a moment when distilling at atmospheric pressure, or by rapidly cooling the distillation flask with an air blast.

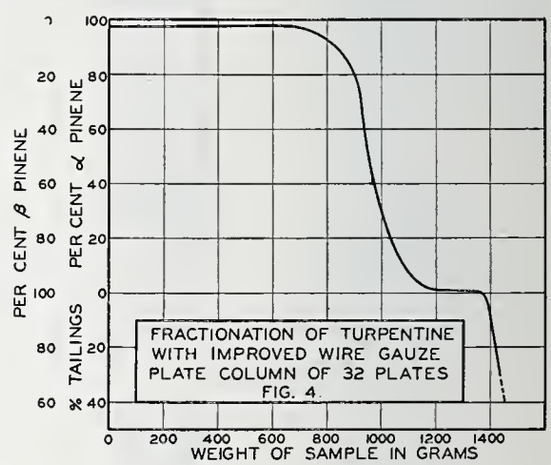
Test distillations were made, at atmospheric pressure, of a mixture of benzene and toluene, and at reduced pressure of a mixture of alpha and beta pinene from turpentine with:

(*a*) Bruun column, 15-plate and approximately 125 cm. long and 2 cm. external diameter.
(*b*) Dupont column, 30-plate and approximately 190 cm. long and 2.5 cm. external diameter.
(*c*) Improved gauze-plate column here described, 15-plate and approximately 110 cm. long and 2.5 cm. external diameter.

The same mixtures were used in the respective columns *a*, *b*, and *c* in equal volumes (500 grams) except in the case of the alpha-beta pinene mixture for column *c*, where only enough of the sample remained to run 300 grams.

The reflux ratio was controlled by an automatic reflux regulator (8*a*) in the Bruun apparatus, and by means of a stopcock in the other columns. All the columns were provided with thermal insulation, and the pressure was controlled with a pressure regulator when fractionating in vacuum.

The results of these runs are shown graphically in Figures 2 and 3.



The data shown in Figure 4 were obtained with a 32-plate gauze-plate column of type *c* on a sample of turpentine which contained 61 per cent alpha pinene, 34 per cent beta pinene, and the remainder "tailings." Composition data for the alpha-beta pinene mixtures were computed from optical rotations of the fractions by the method of Darmois and Dupont (*2*).

These results indicate in a measure the degree of fractionation obtainable by the respective columns. However, in the absence of automatic control of the reflux ratio for the gauze-plate columns, and in view of structural differences in diameter, column length, etc., as indicated above, these results cannot be regarded as exact measures of the relative effectiveness of the respective columns.

Literature Cited

(1) Bruun, Ind. Eng. Chem., Anal. Ed., **1**, 212, Fig. 7 (1929).
(2) Dupont, *Chime industrie*, **8**, 555 (1922).
(3) Hill and Ferris, Ind. Eng. Chem., **19**, 379 (1927).
(4) Marshall and Sutherland, *Ibid.*, **19**, 735 (1927).
(5) Midgely, *Ibid.*, Anal. Ed., **1**, 88 (1929).
(6) Rittmann and Dean, J. Ind. Eng. Chem., **7**, 185 (1915).
(7) Young, "Distillation Principles and Processes," Chap. XI, Macmillan, London, 1922.

Benzidine Method for Determination of Acetic Acid in Lead Acetate[1]

John E. S. Han and T. L. Chu

Y-1065c North Szechuen Road, Shanghai, China

The lead in lead acetate is precipitated by sulfuric acid in the presence of thymol blue until the solution acquires a distinctly red-orange color, indicating the acid range. Alcohol is added and the solution filtered. The excess sulfuric acid is precipitated with benzidine and again filtered. The acetic acid is directly titrated with standard sodium hydroxide to a yellowish green color, indicating the alkaline range. This is a quick method and the results agree closely with the phosphoric acid distillation method. Equally accurate results can be obtained with phenolphthalein as the indicator. Lead can be conveniently determined by heating the lead sulfate precipitate to constant weight.

The standard method for estimating acetic acid in lead and other acetates involves distillation with phosphoric acid (*5*). If the distillation is carried nearly to dryness (*2*), some phosphoric acid usually passes into the distillate. The passing over of phosphoric acid can be reduced to a negligible amount by adding water continuously (*6*, *11*) or intermittently (*5*, *10*) during the process of distillation. The advantage gained in accuracy is offset by the much longer time required for each distillation. Steam distillation (*4*) consumes less time, but some of the phosphoric acid is mechanically carried over (*5*).

Fresenius (*3*) determined acetic acid in lead acetate by adding an excess of standard sulfuric acid, filtering, and titrating an aliquot part of the filtrate. From the total acidity found is deducted that due to the excess sulfuric acid in the filtrate. This requires a separate determination of sulfuric acid. Kolthoff (*8*) found it possible to obtain an accuracy of 0.2 per cent, when acetates of alkalies or alkaline earths are titrated with normal hydrochloric acid using reference solution and tropeolin 00 or thymol blue as indicator. With basic lead acetate, Duchemin and Criqueboeuf (*1*) recommended a previous neutralization with standard acetic acid using phenolphthalein as indicator.

The authors' method consists of precipitating the lead with sulfuric acid, filtering, and washing through a Gooch crucible, precipitating the excess sulfuric acid with an alcoholic solution of benzidine, again filtering, washing, and titrating with standard sodium hydroxide. The titration is a direct measurement of the acetic acid present, and yields equally accurate results with normal and basic lead acetates.

Lead can be conveniently determined by transferring all the lead sulfate onto the Gooch crucible and heating to constant weight in the usual manner. A correction for insoluble matter should be applied when present.

Solutions Required

Carbon Dioxide-Free Water—Ordinary distilled water was boiled in a flask of Jena glass, fitted with a soda-lime tube, and allowed to cool. Carbon dioxide-free water was used exclusively for all work, including preparation of solutions. Gooch crucible sieve plates were used for preventing bumping when water or solutions were boiled.

Containers for volumetric solutions were provided with Popoff (*9*) buret-filling devices and soda-lime tubes.

0.5 *N* and 0.1 *N* Sodium Hydroxide—The sodium carbonate in a stock solution of sodium hydroxide was removed with a slight excess of barium nitrate. A portion of the clear supernatant solution was siphoned off, diluted to the approximately desired normality, and treated with a slight excess of sodium sulfate. The clear solution was siphoned off and standardized against potassium acid phthalate. All siphoning was carried out with the exclusion of carbon dioxide. The containers were heavily paraffined.

0.1 *N* Acetic Acid and 0.2 *N* Sulfuric Acid—These solutions were boiled, cooled under a soda-lime tube, and standardized against the 0.1 *N* sodium hydroxide.

Benzidine Solution—Exactly 9.21 grams of the free base were dissolved in 95 per cent alcohol and diluted to 1 liter.

Phenolphthalein—One gram was dissolved in 100 cc. of 95 per cent neutral alcohol.

Thymol Blue—Exactly 0.12 gram was mixed with 2.84 cc. of 0.1 *N* sodium hydroxide and diluted with water to 100 cc.

Neutral Alcohol—Two hundred and fifty cubic centimeters of 95 per cent ethyl alcohol were neutralized with 0.1 *N* sodium hydroxide, using about 32 drops of thymol blue or 5 drops of phenolphthalein for indicator. Dilute neutral alcohol was prepared by diluting 90 cc. of neutral alcohol with 81 cc. of water.

Benzidine Method with Thymol Blue as Indicator

Procedure—Dissolve 0.94 to 0.95 gram of lead acetate with 20 cc. of water in a 150-cc. beaker. Add 8 drops of thymol blue and sufficient 0.2 *N* sulfuric acid to cause the solution to assume a distinctly red-orange color. (Compare with 45 cc. of 0.1 *N* acetic acid, 1 cc. of 0.2 *N* sulfuric acid, 8 drops of thymol blue, and some pure barium sulfate in a similar beaker. The presence of a white precipitate causes the solution to appear more red.) Introduce 50 cc. of 95 per cent neutral alcohol and allow to stand for 30 minutes. Filter through a Gooch crucible with gentle suction into a 300-cc. Erlenmeyer flask of Pyrex glass. Wash the beaker and crucible with 50 cc. of dilute neutral alcohol. Detach the crucible from the Gooch funnel and wash the funnel and bottom of the Gooch crucible with 25 cc. of water. Add 5 cc. of benzidine solution, mix, and allow to stand for 5 minutes. Filter through a 9-cm. filter paper (S. & S. No. 597), wash with 50 cc. of water, and collect filtrate and washings in a 300-cc. Erlenmeyer flask. It is best to use a long-stem Bunsen funnel, and to fill the stem with water before filling the filter with the alcoholic solution. Titrate with 0.1 *N* sodium hydroxide until the color matches that of a color standard prepared by dissolving 0.06 gram of chromic chloride crystals and 0.0035 gram of potassium chromate in 270 cc. of water.

Discussion—If to 45 cc. of 0.1 *N* acetic acid are added 8 drops of thymol blue, the solution assumes a yellowish orange color. The solution turns more orange and finally to red upon additions of 0.2 *N* sulfuric acid. It is difficult to judge the color change with certainty until about 0.2 cc. of the sulfuric acid has been added. When a white precipitate is present, the color change caused by small quantities of sulfuric acid can be clearly observed only after settling. A distinct orange-red color, however, can be easily observed when an excess of 0.5 to 1.0 cc. of 0.2 *N* sulfuric acid has been introduced. On addition of alcohol, the color of the solution changes to yellow with a faint orange shade. The alcoholic solution changes to a nearly pure yellow color when the excess of sulfuric acid is precipitated by benzidine.

Benzidine sulfate precipitate, when formed in the presence

[1] Received April 22, 1931. Presented before the annual convention of the Chinese Society of Science and Arts, Nanking, December 5, 1930.

of acetic acid, is very fine. On standing, it gradually coagulates into coarser crystals.

To ascertain whether or not this physical difference has any bearing on the purity of the precipitate, various amounts of sulfuric acid were added to 41.60 cc. of 0.10818 N acetic acid, diluted with 75 cc. of 95 per cent alcohol and 95 cc. of water, and treated with benzidine. After filtering and washing with 50 cc. of water, it was titrated with 0.10706 N sodium hydroxide. The results given in Table I definitely show that no acetic acid or benzidine acetate has been carried down by the precipitate.

Table I—Precipitation of Benzidine Sulfate in Presence of Acetic Acid

(41.60 cc. of 0.10818 N AcOH ≈ 42.03 cc. 0.10706 N NaOH)

Experiment	0.2 N H_2SO_4	0.1 N Benzidine	0.10706 N NaOH Required for Titrating Filtrate[a]	Error
	Cc.	*Cc.*	*Cc.*	*Cc.*
1	1	4	42.07	+0.04
			42.03	0.00
2	2	6	42.04	+0.01
			41.98	−0.05
			42.05	+0.02
3	3	8	42.01	−0.02
			42.00	−0.03
4	4	10	42.01	−0.02
			42.06	+0.03
5	1	6	42.04	+0.01
			42.02	−0.01
6	1	12	42.06	+0.03
			42.00	−0.03

[a] Corrected for effect of alcohol on indicator.

If the benzidine sulfate is washed with an additional 50 cc. of water, the washings would require 0.14 to 0.15 cc. of 0.1 N sodium hydroxide for neutralization. Excessive washing should therefore be avoided.

With 5 cc. of 0.2 N sulfuric acid, the precipitate of benzidine sulfate formed was heavy and could be filtered only with difficulty. The presence of alcohol decreases the sharpness of the thymol blue end point, making necessary the use of a color standard. The authors took the first change from yellow to yellowish green as the end point, which can be easily recognized by comparing with the permanent color standard.

Both the 95 per cent and dilute alcohol should be neutralized shortly before use. When many analyses are to be made, ordinary ethyl alcohol might be used, and the amount of 0.1 N sodium hydroxide required for neutralizing 75 cc. of the 95 per cent alcohol deducted from the buret reading. Usually 0.1 to 0.2 cc. of 0.1 N alkali is required, depending on the purity of the alcohol.

Phosphoric Acid Distillation Method

The results of the benzidine method were compared with the phosphoric acid distillation method. The distillation method used was a combination of those of Bayer (*5*) and Scott (*10*).

Procedure—Etch two lines on a 500-cc. round-bottom flask to indicate volumes of 70 and 170 cc., respectively. Introduce 4.1 to 4.2 grams of lead acetate into the flask and dissolve in water, add 0.3 gram of zinc dust and 20 cc. of phosphoric acid (density, 1.7), and then dilute to 170 cc. with water. Insert a rubber stopper which carries a separatory funnel and a Gray's distilling bulb (*7*). The condenser is preferably of the spiral type. Place the round-bottom flask over an asbestos board with a hole in the center. Place 40 cc. of 0.5 N sodium hydroxide in the receiver which is a 1-liter flask of Jena glass. Heat the round-bottom flask with a direct flame. When the liquid is reduced to 70 cc., add hot water from the separatory funnel until it again reaches the 170-cc. line. Repeat the distillation until 800 cc. of distillate have been collected, then change receivers, and boil the 840 cc. of solution in the first receiver with a Gooch crucible sieve plate under a reflux condenser for 20 minutes. Fit a soda-lime tube, cool, and titrate with 0.5 N sodium hydroxide, using about 16 drops of phenolphthalein for indicator. Titrate further distillates until 1 drop of the alkali produces a permanent pink color.

Discussion—Under the conditions of the procedure about 50 per cent of the acetic acid is expelled by each distillation. Thus, in one experiment, the nine successive portions of distillates required for neutralization, 21.33, 10.82, 5.41, 2.46, 1.21, 0.55, 0.24, 0.07, and 0.04 cc. of 0.51597 N sodium hydroxide, amounted to 50.63, 25.68, 12.84, 5.84, 2.87, 1.31, 0.57, 0.17, and 0.09 per cent of the total volume (42.13 cc.) of alkali consumed, respectively. During the experiment, each succeeding portion, together with 2 drops of phenolphthalein, was added to the titrated solution and titration continued. The solution was not boiled, but a correction for carbon dioxide as found in ordinary distilled water was applied. Acetic acid is sometimes completely distilled in the first 800 cc., but it also often happened that 1 or 2 drops of 0.5 N sodium hydroxide are required for the ninth hundred cc. Results obtained with this method are given in Table II.

Table II—Phosphoric Acid Distillation Method

Sample	Wt. of Sample	0.51506 N NaOH	AcOH
	Grams	*Cc.*	%
Lead acetate, Merck's reagent	4.1516	42.09	31.35
	4.1168	41.80	31.40
	4.1127	41.76	31.40
		Av.	31.38
Lead acetate, com'l. crystals, 1	4.1178	41.78	31.38
	4.1525	42.22	31.44
	4.1575	42.21	31.40
		Av.	31.41
Lead acetate, com'l. crystals, 2	4.1178	41.73	31.34
	4.1091	41.67	31.36
	4.1127	41.74	31.39
		Av.	31.36
Lead acetate, pharmaceutical	4.1794	42.30	31.30
	4.1140	41.62	31.29
	4.1015	41.45	31.25
		Av.	31.28
Lead subacetate, Merck	5.9392	47.62	24.80
	5.7460	46.00	24.76
	5.6039	44.80	24.72
	5.4830	43.94	24.78
		Av.	24.76

Table III—Comparison of Phosphoric Acid Distillation Method with Benzidine Method using Thymol Blue as Indicator

Sample	Benzidine Method: Wt. of sample	Benzidine Method: 0.10446 N NaOH[a]	Benzidine Method: AcOH	AcOH by H_3PO_4 Distillation Method	Diff.
	Grams	*Cc.*	%	%	%
Lead acetate, com'l. crystals, 1	0.9453	47.28	31.37		
	0.9468	47.44	31.42		
	0.9453	47.19	31.31		
	0.9420	47.11	31.37		
	0.9471	47.30	31.32		
	0.9477	47.43	31.39		
	0.9444	47.15	31.31		
			Av. 31.36	31.41	−0.05
Lead subacetate, Merck	1.1205	44.17	24.72		
	1.1065	43.80	24.83		
	1.1449	45.07	24.69		
	1.1337	44.64	24.70		
	1.1298	44.62	24.77		
	1.1346	44.63	24.67		
			Av. 24.73	24.76	−0.03

[a] Corrected for effect of alcohol on indicator.

Precipitate of lead phosphate causes considerable bumping. Zinc replaces lead in the phosphate and causes it to separate in a spongy form, and the spongy lead helps to prevent bumping. In case bumping should occur, add a little zinc dust through the separatory funnel with the next portion of water. Obviously the tip of the separatory funnel should not be made too small.

Phosphoric acid often contains volatile acids. The authors used Merck's reagent quality and found that 20 cc. yielded, in 800 cc. of distillate, enough acid to neutralize 0.2 to 0.3 cc.

of 0.1 N sodium hydroxide. The correction for this error is therefore about 1 drop of 0.5 N alkali.

In another series of experiments, water was added to the phosphoric acid left over from a previous blank determination, and distillation continued repeatedly. The acid in each 800 cc. of distillate was titrated and found to require 0.13 to 0.21 cc. of 0.1 N sodium hydroxide. Apparently a minute amount of phosphoric acid has been mechanically carried over in spite of all the precautions taken. The 1 drop of 0.5 N alkali correction, therefore, covers not only volatile acids, but also phosphoric acid carried over mechanically.

A comparison of this method with the benzidine method using thymol blue is given in Table III.

Benzidine Method with Phenolphthalein Indicator

If analysis of lead acetate is made only occasionally, it might not be desirable to prepare a permanent color standard. In such a case, one would find the benzidine method with phenolphthalein as indicator more suitable.

Procedure—Dissolve 0.94 to 0.95 gram of the sample in 20 cc. of water, and add 26 cc. of 0.2 N sulfuric acid and 50 cc. of 95 per cent neutral alcohol. After standing for 30 minutes, filter through a Gooch crucible and wash with 50 cc. of dilute neutral alcohol. Wash the Gooch funnel and the bottom of the crucible with 25 cc. of water. Collect the filtrate and washings in a 300-cc. Erlenmeyer flask of Pyrex glass. Add 5 cc. of benzidine solution and allow to stand for 5 minutes. Filter through a 9-cm. filter paper, and wash with 50 cc. of water. Titrate the filtrate and washings with 0.1 N sodium hydroxide, using 4 drops of phenolphthalein as indicator.

Accuracy of Results—The results obtained with phenolphthalein and thymol blue are equally accurate. Table IV gives the results obtained with five samples of lead acetate.

Discussion—Twenty-six cubic centimeters of 0.2 N sulfuric acid are sufficient for precipitating the lead in 0.9483 gram of lead acetate [$Pb(C_2H_3O_2)_2.3H_2O$], leaving 1 cc. in excess. Practically all the ordinary lead acetate of commerce is of this composition, though often a minute amount of acetic acid has been lost through absorption of carbon dioxide. Loss of part of the water of crystallization also often occurs during storage. More than 26 cc. of the acid would be required if the sample is a basic salt. The failure of benzidine to produce a precipitate shows that an insufficient amount of sulfuric acid has been added. If the lead content is known, the amount of acid to be added can be found by calculation. A separate rough titration with thymol blue will also furnish the necessary information.

The phenolphthalein end point is quite sharp in the presence of alcohol, and no color standard is required.

Table IV—Benzidine Method with Phenolphthalein Indicator

Sample	Benzidine Method: Wt. of sample	0.10706 N NaOH	AcOH	AcOH by H_3PO_4 Distillation Method	Diff.
	Grams	*Cc.*	%	%	%
Lead acetate, Merck's reagent	0.9463	46.09	31.31		
	0.9431	46.00	31.35		
	0.9474	46.19	31.34		
			Av. 31.33	31.38	−0.05
Lead acetate, com'l. crystals, 1	0.9474	46.30	31.41		
	0.9464	46.22	31.39		
	0.9421	45.92	31.33		
			Av. 31.38	31.41	−0.03
		(0.10026 N)			
Lead acetate, com'l. crystals, 2	0.9467	49.34	31.37		
	0.9445	49.25	31.39		
	0.9476	49.16	31.23		
			Av. 31.33	31.36	−0.03
Lead acetate, pharmaceutical	0.9457	49.02	31.20		
	0.9415	48.97	31.31		
	0.9446	49.15	31.32		
			Av. 31.28	31.28	−0.00
Lead subacetate, Merck	0.9272	38.22	24.81		
	1.1619	47.58	24.65		
	1.1245	46.24	24.75		
			Av. 24.74	24.76	−0.02

Acknowledgment

The authors are indebted to G. A. Haley, T. W. Zee, A. T. Bawden, and J. W. Gibb for reading over the manuscript and offering valuable suggestions.

Literature Cited

(1) Duchemin and Criqueboeuf, *Bull. assocn. chim. sucr. dist.*, **24**, 1216 (1907).
(2) Fresenius, *Z. anal. Chem.*, **5**, 315 (1866).
(3) Fresenius, *Ibid.*, **13**, 30 (1874).
(4) Fresenius, *Ibid.*, **14**, 172 (1875).
(5) Fresenius and Grünhut, *Ibid.*, **47**, 597 (1908).
(6) Gladding, J. Ind. Eng. Chem., **1**, 250 (1909).
(7) Gray, *Ibid.*, **1**, 802 (1909).
(8) Kolthoff, *Z. anorg. allgem. Chem.*, **115**, 168 (1921).
(9) Popoff, "Quantitative Analysis," 2nd ed., p. 71, Blakiston, 1927.
(10) Scott, "Standard Methods of Chemical Analysis," 4th ed., Vol. II, p. 1547, Van Nostrand, 1927.
(11) Stillwell and Gladding, *J. Soc. Chem. Ind.*, **23**, 305 (1904).

Stability of Potassium Ferrocyanide Solutions[1,2]

I. M. Kolthoff and E. A. Pearson

University of Minnesota, Minneapolis, Minn.

In connection with work on the use of potassium ferrocyanide solutions as a reagent in volumetric procedures, considerable difficulty was encountered on account of the instability of the solutions (1/40 molar) with or without some potassium ferricyanide.

The decomposition of potassium ferrocyanide solutions when exposed to light or to air or to both has been the subject of many investigations (*1–3, 5–7, 9–15, 17–19, 21*). However, the total mechanism of the various steps in the decomposition reaction are still not clearly understood. It has been known for some time that a fresh solution of potassium ferrocyanide in water does not redden phenolphthalein; on standing in light it is colored red. If this solution is allowed to stand in the dark, the color again disappears. Therefore, it was thought that the first stage of the decomposition could be represented by the following reversible reaction:

$$2Fe(CN)_6^{----} + {}^1/_2O_2 + H_2O \underset{\text{light}}{\overset{\text{dark}}{\leftrightarrows}} 2Fe(CN)_6^{---} + 2OH^-$$

Jimori (*8*), however, showed that the reaction proceeds in the light without oxygen, and that in the first stage of the decomposition aquopentacyanide is formed which has a yellow color:

$$Fe(CN)_6^{----} \leftrightarrows Fe(CN)_5^{---} + CN^-$$
$$Fe(CN)_5^{---} + H_2O \rightarrow (Fe(CN)_5H_2O)^{---}$$
$$CN^- + H_2O \leftrightarrows HCN + OH^-$$

or summarized:

[1] Received May 29, 1931.

[2] Part of a thesis submitted by E. A. Pearson to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of doctor of philosophy.

Table I—Decomposition of 1/40 *M* Potassium Ferrocyanide at Room Temperature

Expt.	Temp. of Recrystallization of Ferrocyanide °C.	Solvent	Color of Glass of Bottle	Decrease in Strength after 16 Days	Decrease in Strength after 37 Days	Remarks
1	100	Distilled water, pH 5.2	Colorless	1.7	7.4	Soln. dark yellow; precipitate of Fe_2O_3 on bottom
2	100	Distilled water, pH 5.2	Brown	0.8	1.1	Soln. bright yellow; no turbidity
3	100	Conductivity water, pH 6.5	Brown	0.3	0.7	Soln. bright yellow; no turbidity
4	80	Distilled water, pH 5.2	Brown	1.3	1.7	Soln. bright yellow; no turbidity
5	80	Conductivity water, pH 6.5	Colorless	1.5	4.8	Soln. dark yellow; precipitate of Fe_2O_3 on bottom
6	80	Conductivity water, pH 6.5	Brown	0.6	0.6	Soln. bright yellow; no turbidity or deposit
7	100	Distilled water + 0.1% sodium bicarbonate	Brown	0.4	0.6	Soln. bright yellow; no turbidity or deposit
8	80	Distilled water + 0.1% sodium bicarbonate	Brown	0.5	0.9	Soln. bright yellow; no turbidity or deposit
9	100	Distilled water + 0.2% sodium carbonate	Brown	0.0	0.0	Practically colorless after 1 day; slightly yellow after 37 days
10	80	As 8	Brown	0.0	0.0	Practically colorless after 1 day; slightly yellow after 37 days
11	100	Distilled water + 0.1% sodium hydroxide	Brown	0.0	+0.4	Soln. colorless; ferric hydroxide on bottom
12	80	As 11	Brown	0.0	−0.4	Soln. colorless; ferric hydroxide on bottom
13	100	Conductivity water + 0.3% potassium ferricyanide	Brown	1.0		
14	80	As 13	Brown	0.9		
15	80	Distilled water + 0.2% sodium carbonate and 0.2% $K_3Fe(CN)_6$	Brown	0.0	0.0	
16	100	As 15	Brown	0.0	+0.3	

$$Fe(CN)_6^{----} + 2H_2O \rightarrow [Fe(CN)_5H_2O]^{---} + OH^- + HCN$$

Heat and sunlight favor the decomposition; at low temperatures and in the dark the reverse reaction takes place. The subsequent steps in the decomposition according to Jimori are non-reversible, and in the presence of oxygen lead to the formation of iron oxide and cyanic acid.

From the analytical point of view it is interesting to note that the first stage of the decomposition is reversible, and from the reaction mechanism it may be expected that an excess of hydroxyl ions will prevent the formation of the aquopentacyanide. Therefore, it may be anticipated that the stability of a ferrocyanide solution will depend largely on the pH of the solution. This was experimentally confirmed. In the beginning of this work 1/40 molar solutions of pure potassium ferrocyanide were prepared in ordinary distilled water having a pH of 5.0 to 5.4. This water contains more carbon dioxide than is in equilibrium with the air. The strength of the solution decreased 0.4 per cent one day after the preparation, and the decomposition proceeded on longer standing. When conductivity water with a pH of 6.0 to 6.7 was used as a solvent, the decomposition was much less, but still amounted to 0.5 per cent after 3 days' standing in diffuse light. In all cases direct sunlight favored the decomposition very much.

It was thought necessary to make a more extensive investigation of the stability of ferrocyanide solutions in order to get a reagent which does not change on standing. Some of the results are given. (Only part of the work will be given here. For more details the reader is referred to the thesis of E. A. Pearson.)

Potassium Ferrocyanide Used

The higher the temperature of recrystallization of the ferrocyanide the more aquopentacyanide is formed, according to Briggs (*4*). Schröder (*20*) stated that potassium ferrocyanide may be satisfactorily crystallized from a boiling, saturated solution. Some hydrocyanic acid is formed, but the salt when thus recrystallized always had a normal water content, contrary to the statement of Müller and Diefenthaler (*16*). The results in this laboratory showed only slight differences in the progressive decomposition of salts recrystallized at 80° and at 100° C. but undoubtedly more aquopentacyanide is formed at higher temperatures, for the salt recrystallized from boiling solutions had a slightly more yellowish tinge. Also, solutions made from such salts seemed to be initially more yellow. Moreover, such solutions when stabilized with alkali and kept in the dark appeared to gain slightly in strength (0.1 to 0.3 per cent in 3 days) owing to the driving back of the hydrolysis, and coincidentally the solutions became almost colorless.

In the following experiments, shown in Table I, two samples of potassium ferrocyanide were used. Two samples of analytical-grade ferrocyanide recrystallized at 80° to 90° C. were recrystallized, one at 80° C. and the other by saturating at boiling temperature by the method of Schröder. In the latter case the solution was maintained at boiling for 3 minutes, then filtered, and allowed to crystallize.

Stability of Ferrocyanide Solutions—Portions of 200 to 250 cc. of the 1/40 molar solutions were placed in well-stoppered flasks and exposed to laboratory light. During the last 21 days of the experiment (January), the bottles were kept on the window sill facing the sun. The analysis of these solutions was performed by pipetting out 25 cc., adding 10 cc. of 4 *N* sulfuric acid, one drop of 1 per cent potassium ferricyanide, 3 drops of 1 per cent diphenylamine, and titrating with 0.025 *M* zinc sulfate until the yellowish green color changed to bluish purple.

From these and many other experiments the following conclusions may be drawn:

(1) Ferrocyanide solutions kept in transparent bottles are much less stable than those in brown bottles when exposed to light.

(2) The stability of the solution decreases with increasing acidity. In distilled water with an excess of carbon dioxide (pH 5.0 to 5.2), the decomposition is stronger than in water which is in equilibrium with the air.

(3) The method of recrystallization of the ferrocyanide has no appreciable effect upon the stability of the solution.

(4) The presence of small amounts of ferricyanide favors the decomposition of ferrocyanide solutions.

(5) Dilute solutions are relatively less stable than more concentrated solutions.

(6) Solutions prepared in 0.2 per cent sodium carbonate in distilled water are stable for long periods of time. Change of the temperature (up to 50° C.) and presence of small amounts of ferricyanide have no or little effect upon the stability in this alkaline medium.

Literature Cited

(1) Baudisch, *Ber.*, **62**, 2706 (1929).
(2) Baudisch and Bass, *Ibid.*, **54**, 413 (1921); **55**, 2698 (1922).
(3) Bauer, *Helv. Chim. Acta*, **8**, 403 (1900).
(4) Briggs, *J. Chem. Soc.*, **93**, 1571 (1908); **99**, 1019 (1911); **117**, 1026 (1920).
(5) Donath and Hottenhauser, *Chem.-Ztg.*, **14**, 323 (1890).
(6) Haber, *Z. Elektrochem.*, **11**, 846 (1905).
(7) Haber and Foster, *Chem.-Ztg.*, **29**, 652 (1905); *J. Chem. Soc.*, **89**, 912 (1906).
(8) Jimori, *Z. anorg. allgem. Chem.*, **167**, 145 (1927).
(9) Kistiakowsky, *Z. physik. Chem.*, **35**, 431 (1900).
(10) Kolthoff, *Z. anorg. allgem. Chem.*, **110**, 147 (1920); "Volumetric Analysis," Vol. I, Wiley, 1928.
(11) Kolthoff and Verzyl, *Rec. trav. chim.*, **43**, 380 (1924).
(12) Koninck, de, and Prost., *Z. angew. Chem.*, **15**, 460, 564 (1896).
(13) Luckow, *Chem.-Ztg.*, **15**, 1491 (1891).
(14) Matuschek, *Ibid.*, **25**, 565 (1901).
(15) Modenhauer, *Ibid.*, **15**, 223 (1891).
(16) Müller and Diefenthaler, *Z. anorg. Chem.*, **67**, 421 (1910).
(17) Rossi and Bocchi, *Gazz. chim. ital.*, **55**, 816 (1925).
(18) Schaum and van der Linde, *Z. Elektrochem.*, **9**, 406 (1903).
(19) Schönbein, *Fortschritt Physik*, 228 (1846).
(20) Schröder, *Z. anorg. allgem. Chem.*, **72**, 89 (1911).
(21) Walker, *J. Am. Chem. Soc.*, **23**, 468 (1901).

A Simple and Easily Constructed Gas-Pressure Regulator[1,2]

A. C. Robertson

University of Illinois, Urbana, Ill.

During the course of an investigation concerning combustion, it became necessary to burn very small amounts of city gas at a constant rate. The supply pressure sometimes ranged as high as 16 inches water column and made the problem of governing the pressure a little more difficult than usual. The customary form of gas-pressure regulator, such as those used for the purposes of gas calorimetry, was found to be unsuitable for handling small quantities of gas, permitting enough increase in pressure to nullify its usefulness entirely. Upon considering the construction of the pressure regulator being used, it became apparent that the design was faulty, and that repairing or adjusting the device would not correct its faults. Regulators of this sort are designed to handle gas in the quantities needed for calorimetry and cannot be expected to control minute amounts.

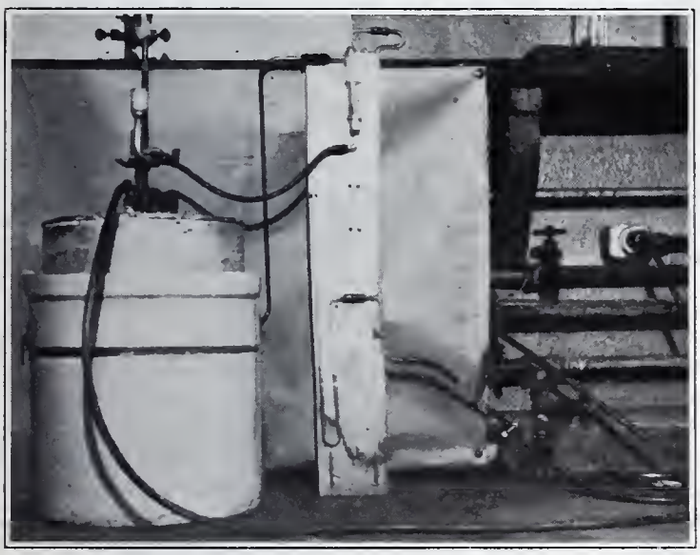


Figure 1—Large Size Gas Regulator

A pressure regulator was accordingly extemporized from materials easily available in the laboratory in an attempt to avoid the recognized difficulties. The new form of regulator has worked so reliably and so successfully that the author wishes to describe it even though it is so simple that it has possibly been used before. A cursory search of the usual literature has revealed no description of a similar device, and hence the following details are submitted in the hope that others will find the apparatus useful. It may be constructed on a small scale when exact pressure regulation is not vital, but is better made larger, when regulation is very exact and free from rapid fluctuations. The larger container is therefore described, and illustrated in Figure 1.

A 4-gallon (15-liter) crock was used for the outer container which holds a "bell" consisting of a metal can 10 inches (25.4 cm.) in diameter having soldered to its top a boss for holding in an axial position $^5/_{16}$-inch (0.79-cm.) rod which serves as a guide. A small petcock soldered to the top of the can near its edge serves as an outlet for the gas. The inlet consists of an elongated S-shaped glass tube which fits loosely between the bell and the walls of the crock. This tube with two other tubes, having hooked ends to fit over the edge of the crock, serve as guides to prevent the bell from rubbing against the sides of the outer container. One of these tubes could be used for an outlet tube, but this is not advisable since condensate may collect in it and obstruct the flow of gas. The guide rod on the top of the bell passes through a short sleeve of loosely fitting glass tubing with fire-polished ends. The guide may be fastened to a shelf or to a ringstand which may also serve to support the valve mechanism.

The regulating mechanism is simple. It consists of a glass tube, with a small bulb to catch any overflow of mercury, fastened to the bell or the guide rod and connected by small gum tubing to the valve chamber proper. In the simplest form the valve consists of a tube which has a bottom entrance for the leveling connection, a side arm for the exit gas, and an axial entrance tube for the gas supply. The mode of operation is as follows: The bell, being full of gas, is emptied in use and descends. In doing so, it lowers the level of the mercury in the valve and leveling tube to such an extent that the inlet port is uncovered and the gas is fed through the valve into the bell, which thereby rises and forces the level of mercury above the entrance port again. The cycle repeats itself as demand is made upon the reservoir. The pressure upon the exit side of the bell is governed by its weight per unit area and remains very constant. Indeed when the load is proportioned to the size of

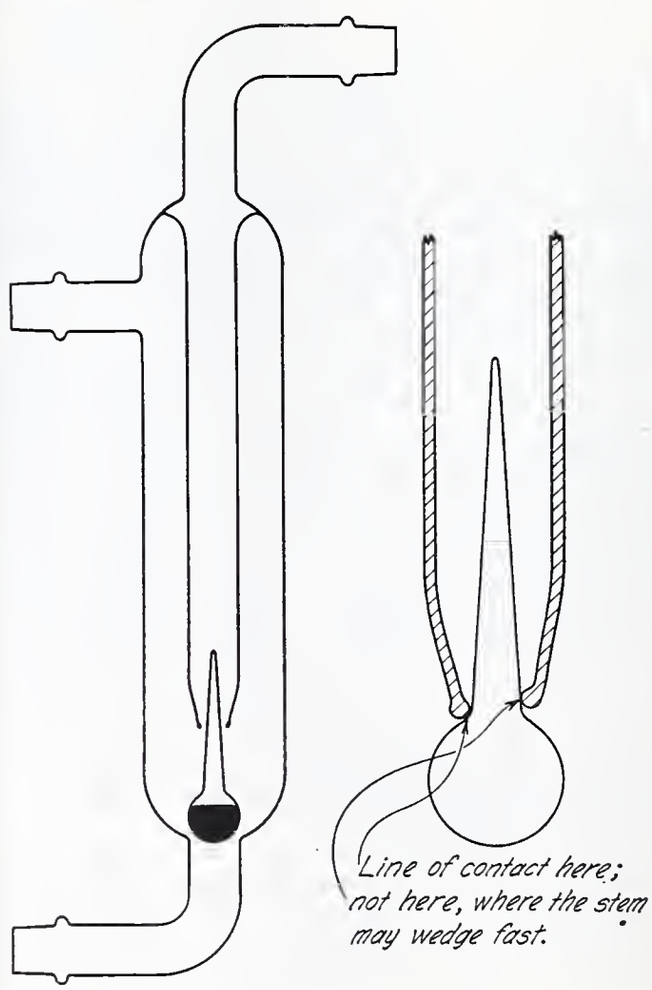


Figure 2—Shape of Valve

[1] Received May 18, 1931.

[2] Published by permission of the Director of the Engineering Experiment Station, University of Illinois.

the bell, a pressure can be maintained constant to about 0.02-inch (0.05-cm.) water column, although when the load is large and fluctuating the variation may reach 0.15-inch (0.38-cm.) water column, depending upon the resistance of the piping at higher velocities of flow.

When much gas is being used or the difference of pressure between the entrance and exit sides is great, the mercury within the valve may be sprayed about violently by the stream of gas passing through the nearly closed entrance port. Therefore, it is well to make a float carrying a needle which will reduce the flow of gas just before the cut-off is complete. The shape of the valve is shown in Figure 2. Care must be taken that the needle makes contact at the points indicated and that the valve cannot jam in any position when the surfaces are finally ground to a fit. The needle is loaded with mercury so that its weight will pull it out of the seat promptly. The needle valve will generally stop the flow of gas as well as throttle it, but if contact is not perfect there will be some leakage past the ground surfaces. Therefore, the distance from the entrance port to the side arm must be such that the mercury column between these points will exert a pressure greater than that produced by any anticipated load.

The regulator described above has several advantages. The valve will not stick or leak, allowing the pressure to build up gradually to a high value when the rate of withdrawal of gas is slight. The pressure is so very constant for small loads that it is quite practical to do away with the use of flowmeters and to use calibrated capillary tubes in their place. The crockery container is immune from corrosion and easily obtained in nearly all laboratories; no special fittings are needed, and a cylindrical tin can will serve as well for the bell as a special container. A large beaker or battery jar may have a guide rod cemented to its base with de Khotinsky cement. When glass is used, a buoyancy effect can be noticed, whereby the pressure of the gas within the bell shows a slight dependency upon the position of the bell instead of being virtually independent of its position, as is the case when iron is used for the material of construction. The most difficult operation involved in the construction of this device is the preparation of the ground joint and inner seal, a construction which is much simplified if Pyrex glass is used for this purpose. Soft glass is preferable for the needle valve.

By the use of two such regulators, it is possible to mix gases in any proportion and to change the ratio easily. The enrichment of a fuel gas with sulfur may be taken as an example. One regulator, for the main supply, operated at 4-inch (10-cm.) water column pressure. Another regulator, working at 6-inch (15-cm.) water column, saturated the gas with carbon bisulfide by passing it over the liquid held in a constant-temperature bath. The enriched gas was led into the main stream through a fine capillary tube whose size was found by trial. After the sulfur content was found by analysis, other concentrations could be secured rapidly by substituting measured lengths of the same capillary tube.

Anodic Precipitation of Lead Peroxide[1]

M. L. Nichols

Department of Chemistry, Cornell University, Ithaca, N. Y.

IT HAS long been known that the best method for the electrolytic determination of lead is by the anodic precipitation of lead peroxide from a solution containing fairly large amounts of nitric acid. All of the conditions governing the accuracy of this determination, including the current density, temperature, presence of other metals and acids, method and temperature of drying, etc., have been the subject of numerous investigations, but little has been done to explain the mechanism of this precipitation.

In the book by Classen (*2*) we find the following statement: "Two explanations have been suggested to account for the formation of the lead peroxide, neither of which is entirely satisfactory. According to Liebenow, the bivalent lead ions are oxidized to negatively charged PbO_2^{--} anions, which are discharged at the anode. Another explanation is that lead tetranitrate is formed by anodic oxidation and from this lead peroxide is formed by hydrolysis. It is not easy to determine whether the mechanism of the reaction is correctly explained by either of these assumptions." Fischer and Schleicher (*3*) state that, in order to explain the inclusion of water, nitric acid, and other components of the electrolyte in the precipitated lead peroxide, the divalent lead ion is oxidized at the anode to tetravalent. The so-formed $Pb(NO_3)_4$ is hydrolyzed to $Pb(OH)_4$ and HNO_3, and the $Pb(OH)_4$ then splits off water and is pressed against the anode by cataphoresis. Vortmann (*7*) had much the same idea.

However, Töpelmann (*6*) says that the divalent lead ion is oxidized at the anode to a tetravalent lead ion, which reacts immediately after its formation with water forming lead peroxide, and the latter, with partial dehydration, will be pressed against the anode by cataphoresis. He also states that the intermediate formation of lead tetranitrate from the tetravalent lead ion and nitric acid plays a very subordinate role.

Jewett (*4*) also believes that the lead is oxidized to negatively charged lead peroxide, and that this is carried against the anode by cataphoresis as there is no way that lead ions can be carried to the anode and no reason at present to assume the existence of any appreciable amount of lead as part of a complex anion. Consequently, the only lead ions that can be oxidized to tetravalent lead are those which happen to be at any moment in contact with the anode.

Experimental Procedure

A solution of lead nitrate was prepared from Kahlbaum's pure crystalline salt, recrystallized several times from water, and the solution standardized by electrolysis according to the method recommended by Töpelmann (*6*). A mixture of 20 ml. of this solution, together with 5 ml. of a solution of copper nitrate (200 grams per liter) and 100 ml. of nitric acid (1 to 4) was diluted to 200 ml. and electrolyzed at room temperature with 1 amp. for 30 minutes. A platinum gauze cathode and a cylindrical platinum gauze anode rotating at 500 r. p. m. and having an area (*1*) of 50 sq. cm. was used. The lead peroxide was washed with water and alcohol, and dried for 1 hour at 190° to 200° C. 20 ml. of the lead nitrate solution gave 0.2138 gram of lead peroxide. When the electrolyte was stirred at 500 r. p. m. with both the anode and cathode stationary, the same result was obtained if the time of electrolysis was increased to 1 hour.

In order to determine whether the lead is carried to the anode by electrolysis or mechanically, the above experiment was repeated with the anode enclosed in a parchment diffusion thimble and all of the lead nitrate in the cathode compart-

[1] Received March 6, 1931. Resubmitted May 25, 1931.

ment. In this case two runs gave only 0.0046 gram and 0.0038 gram, or an average of 0.0042 gram of lead peroxide deposited in 1 hour. This small amount of lead peroxide precipitated is undoubtedly due to diffusion (*5*) of the catholyte into the anode chamber, as some diffusion will take place in all, but quite exceptional, circumstances.

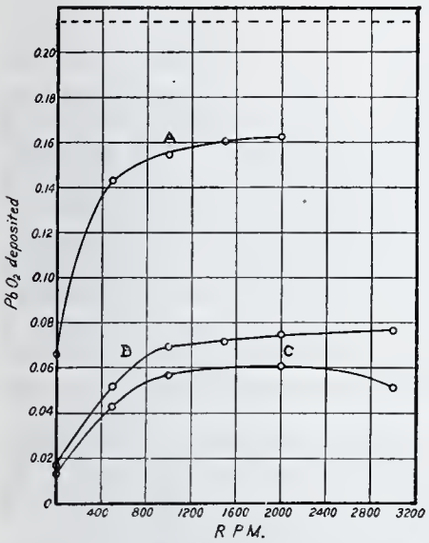


Figure 1—Results of Electrolysis under Various Conditions

If the lead is carried to the anode mechanically, as indicated by the previous experiment, then the rate of precipitation should increase with increased rate of stirring. All conditions were kept the same as in the standardization of the solution, except that the electrolysis was run at 0.25 amp. for exactly 15 minutes of different rate of rotation of the anode. The results are given in Table I and curve A, Figure 1.

If the lead, after being carried to the anode mechanically, is oxidized to negatively charged lead peroxide and carried against the anode by anaphoresis, then it should be possible to increase the rate of stirring to a point where, after the lead is oxidized to lead peroxide, the rotation of the anode would throw it away before it could be pressed against the anode. This should result in a decreased rate of precipitation at very rapid rates of stirring. The previous experiment does not show this effect, since the electrolysis was made in a cell where any negatively charged lead peroxide that was thrown away from the anode would immediately be thrown back against it. If this is the correct reason, then if the electrolysis were carried out in such a manner that the lead peroxide once oxidized could be removed from the cell before it was thrown back against the anode, the decrease should be obtained.

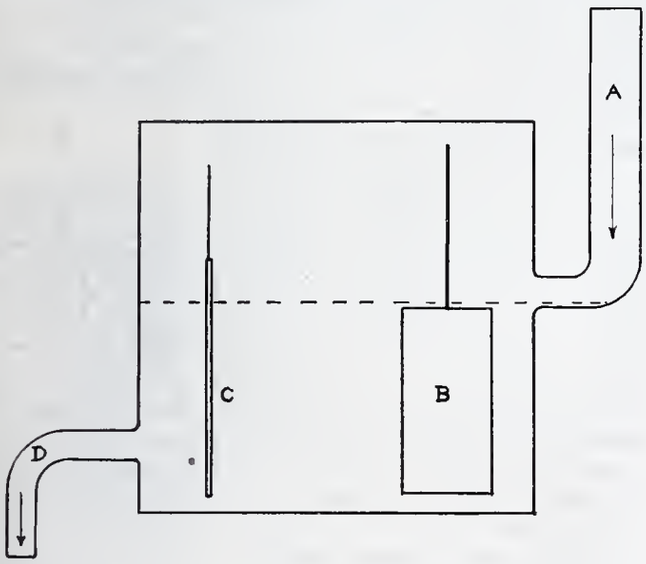


Figure 2—Special Cell for Electrolysis of Lead

Using a solution of the same concentration as in the previous experiments, the electrolysis was carried out in the cell shown in Figure 2. The electrolyte entered through tube *A*, flowed past the anode *B* and the cathode *C*, and then out through *D* at the rate of 545 ml. per minute. Under these conditions the electrolysis was carried out for exactly 5 minutes at 0.5 amp. with the anode rotating at varying rates of speed. The results are given in Table II and curve B, Figure 1.

This experiment did not show the desired result, which was thought to be due to the fact that the rate of flow of the electrolyte was not high enough in proportion to the rate of precipitation of the lead peroxide. The experiment was therefore repeated using the same electrolyte, a current of 1.75 amp., and electrolyzing for exactly 3 minutes with a platinum gauze anode having an area (*1*) of 95 sq. cm. The results are given in Table III and curve C, Figure 1.

Table I—Results of Electrolysis with Ordinary Cell

Rate of Rotation	Lead Peroxide 1	Lead Peroxide 2	Av.
R. p. m.	*Gram*	*Gram*	*Gram*
0	0.0659	0.0655	0.0657
500	0.1430	0.1430	0.1430
1000	0.1543	0.1545	0.1544
1500	0.1617	0.1599	0.1608
2000	0.1621	0.1620	0.1621

Table II—Results of Electrolysis with Special Cell

Rate of Rotation	Lead Peroxide
R. p. m.	*Gram*
0	0.0166
500	0.0517
1000	0.0690
1500	0.0711
2000	0.0746
3000	0.0763

Table III—Results of Electrolysis with Special Cell and Changed Conditions

Rate of Rotation	Lead Peroxide 1	Lead Peroxide 2	Av.
R. p. m.	*Gram*	*Gram*	*Gram*
0	0.0130	....	....
500	0.0426	....	....
1000	0.0562	....	....
2000	0.0609	0.0605	0.0607
3000	0.0526	0.0489	0.0509

Discussion

These results confirm the conclusion of Jewett (*4*) that the lead is not carried to the anode as ion but is merely brought in contract with the anode by stirring the solution. If the lead is first oxidized to $Pb(NO_3)_4$ and then the lead peroxide formed from this by hydrolysis, it should be rather easy to decrease the rate of deposition of the lead peroxide with high rates of anode rotation, as the hydrolysis would take an appreciable time. Since this was not the case, Töpelmann's (*6*) conclusion that the intermediate formation of $Pb(NO_3)_4$ plays a very subordinate role is confirmed. It appears, therefore, that the anodic precipitation of lead peroxide occurs by the lead being mechanically carried to the anode, there oxidized to negatively charged lead peroxide (*8*), and this then pressed against the anode by anaphoresis. This explains why a rough-surfaced anode must be used, and since the negatively charged lead peroxide is probably a hydrous oxide (*8*), the difficulty of removing the last traces of water in the drying of this precipitate (*6*) is readily understood.

Literature Cited

(1) Classen-Boltwood, "Quantitative Chemical Analysis by Electrolysis," p. 114, Wiley, 1903. (Formula given should be area = 2 *dlb* $\sqrt{n}$.)
(2) Classen-Hall, "Quantitative Analysis by Electrolysis," p. 193, Wiley, 1919.
(3) Fischer and Schleicher, "Elektroanalytische Schnellmethoden," p. 244, Enke, 1926.
(4) Jewett, *J. Phys. Chem.*, **33**, 1024 (1929).
(5) Sand, *J. Chem. Soc.*, **93**, 1589 (1908).
(6) Töpelmann, *J. prakt. Chem.*, **121**, 289 (1929).
(7) Vortmann, *Ann.*, **351**, 283 (1907).
(8) Weiser, "Hydrous Oxides," p. 230–231, McGraw-Hill, 1926.

Solid Carbon Dioxide in Laboratory Technic[1]

D. H. Killeffer

DryIce Corporation of America, 52 Vanderbilt Ave., New York, N. Y.

NUMEROUS conditions of crystallization and vapor pressure not easily obtained at the lowest temperatures produced by customary freezing mixtures can be reached in laboratory practice by the use of solid carbon dioxide, now available throughout the United States under the trade-mark "Dry-Ice." The introduction of solid carbon dioxide for commercial refrigerating purposes and its manufacture on a large scale at many points has justified a careful analysis of its possibilities for laboratory use in producing cold. Not only is the commercial material, which is pure carbon dioxide, more convenient to use than small amounts of

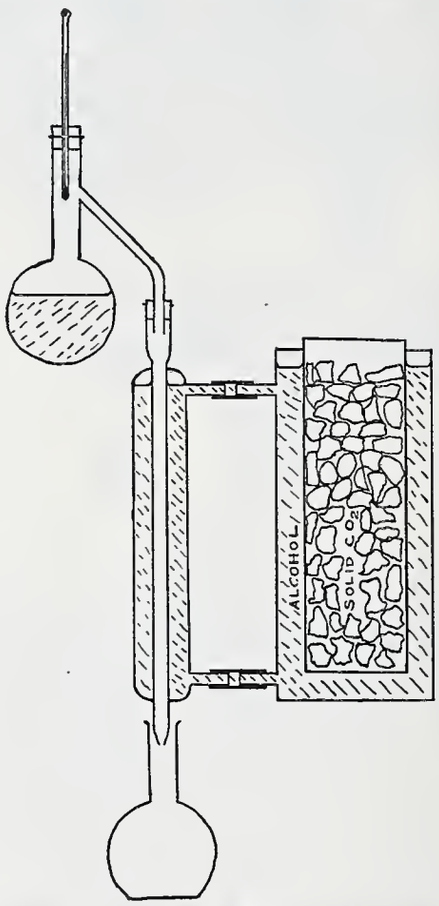


Figure 1—Condensing System Using Solid Carbon Dioxide

snow laboriously solidified in the laboratory, but its cost is actually lower even than that of the liquid carbon dioxide used as the raw material for its small-scale preparation.

It is easily possible with solid carbon dioxide to produce temperatures as low as its normal sublimation point, −78.5° C., and by proper manipulation considerably lower temperatures, down to −100° C., can be reached without great difficulty. Although this range is not as low as that obtainable with liquid air, it does reach a point where practically all common solvents, and many not so common, are either below their freezing points or so close to them that their vapor pressures are negligible.

The influence of such reduced temperatures particularly affects solubilities and vapor pressures. Unlike water, alcohol, ether, and many other solvents pass 0° C. without a break in either solubility or vapor pressure curves, and whatever water may be present in them is still held in solution to much lower temperatures.

Many crystallizations of delicate or low-melting materials, when conducted at the very low temperatures producible with solid carbon dioxide, can be effected easily and much more completely than at higher points. The wider spread of temperature possible in this way greatly increases the yield of crystals per crop, reducing the residue in the mother liquor without requiring evaporation of the solvent. Not only can the crop be increased, but by proper precautions the rate of cooling can be so adjusted as to produce crystals of the most desirable size, a result much less easily obtained by evaporation of the solvent.

Perhaps the most spectacular application of this technic, and one easily carried out for demonstration purposes, is the crystallization of water itself from such solvents as ether or acetone. At solid carbon dioxide temperatures, −78.5° C., the solubility of water in ether is so low that the ether poured off from water crystals will no longer give a positive test for water with anhydrous copper sulfate. Although no accurate determination has been made of residual moisture, it is apparent from boiling-point curves of ether thus treated that a result is attained which will answer many of the practical purposes served by dehydration with metallic sodium and subsequent distillation. A similar, but less complete, dehydration is effected with acetone.

Numerous crystallizations and separations of delicate materials and resinous mixtures may be similarly accomplished with greater facility at low temperature.

Low-temperature distillations under vacuum are of limited application under ordinary circumstances because of the relatively high vapor pressure of many organic materials at ice-bath temperatures. By greatly increasing the temperature range through the use of "Dry-Ice" (either directly or indirectly) to cool condensers and receivers, this limitation can be materially modified. Evans, Cornish, and Atkinson (*1*) have recently discussed a method used by them in evaporating water from biological solutions at low temperatures. For their purposes the evaporation was best accomplished at the lowest possible temperature. The rate is limited by the vacuum obtainable, which in turn is limited by the vapor pressure of the condensed water. By using solid carbon dioxide to cool the receiver and condenser, the effective vapor pressure of the condensate can be made so low that only a negligible amount of water vapor will have to be handled through the vacuum pump.

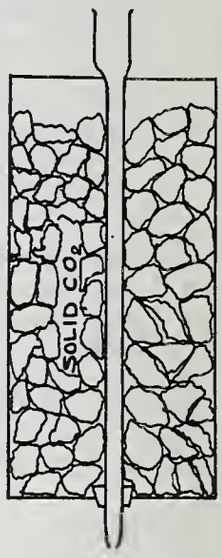


Figure 2—Set-Up of Condenser to Produce Rapid Cooling

Similarly, more volatile solvents than water can be distilled in vacuum and recovered from a solution at or below 0° C., if the condenser and receiver temperature is kept low enough to prevent their evaporation.

The recovery of volatile solvents which may be valuable themselves or which may be hazardous if allowed to escape (ether, carbon bisulfide, etc.), is easily accomplished by the low condenser temperatures thus produced.

[1] Received June 5, 1931.

In distillations, cooling of condensers with solid carbon dioxide must be done in such a way as to prevent or minimize freezing of the distillate on the condensing surface. Water, mercury, carbon tetrachloride, and even anhydrous ammonia freeze at "Dry-Ice" temperatures, and consequently the design of condensers for handling them must be such that freezing will not clog condensate passages or unduly reduce the heat-transfer rate at the cold surface. An arrangement, which allows the liquid to flow readily off the condensing surface into a receiver to be further cooled, is advantageous where there is danger of freezing the distillate.

A number of solvents, especially ether, alcohol, acetone, carbon disulfide, and others are still liquid at −78.5° C. and can be easily handled through such a low-temperature condensing system. Figure 1 shows a suggested condensing system, in which a temperature of −20° C. was reached in the condenser jacket. That shown in Figure 2 produces very low temperatures, down to −78.5° C.

The dehydration of low-freezing solvents by cold and the crystallization of other materials from them has already been suggested above. The technic of doing this is very simple and will readily occur to the investigator. To produce rapid cooling, a slush of solid carbon dioxide in alcohol or ether is placed in a convenient receptacle, preferably a vacuum jar (Pyrex glass), and the solution to be cooled in a convenient container is placed in the mixture. Where slower cooling is required, "Dry-Ice" in small pieces without a solvent may be used and a double-walled vessel for the solution to be cooled still further prolongs the cooling period if this is desired.

The application of extreme cold in the separation of mixtures of materials of widely different freezing points in this way offers many possibilities of value. The removal of fats from alcohol solutions of perfume concretes has been commercially practiced for some time. The separation of benzene from a mixture with ether and many other similar operations can be readily accomplished by crystallization at very low temperatures.

The use of solid carbon dioxide as a condensing or carbon-cooling agent in the production of high vacua with mercury-diffusion pumps is more convenient and cheaper than the use of liquid air and is being widely adopted.

Dehydration of gases to an extent attainable only by the most careful use of chemical dehydrating agents, and the separation of many low-boiling hydrocarbons and other compounds from gases is conveniently accomplished by passing the gas through a glass or metal condenser cooled by solid carbon dioxide either alone or mixed into a slush with alcohol or ether.

Safe storage of products sensitive to oxidation but not injured by carbon dioxide can sometimes be best accomplished by carbonation with "Dry-Ice." Thus, some years ago samples of cracked petroleum distillate very sensitive to light and oxygen were stored in carbonated-beverage bottles, dropping into each 6-ounce sample approximately 3 grams of "Dry-Ice" before capping with an ordinary carbonated beverage crown. So far as the changes in color and gum formation would indicate, oxygen elimination was probably complete.

These possibilities are outlined here to point out the convenience in laboratory practice of this commercial product and to suggest ways in which it can be usefully applied.

Literature Cited

(1) Evans, Cornish, and Atkinson, *J. Am. Chem. Soc.*, **52**, 4334 (1930).

Determination of Butyl and Ethyl Alcohols in Mixtures[1]

C. H. Werkman and O. L. Osburn

Department of Bacteriology, Iowa State College, Ames, Iowa

Ethyl and butyl alcohols are readily and accurately determined by oxidation by potassium dichromate in acid solution to the corresponding acids and quantitative determination of the acids by the partition method. The method is designed for quantitative determinations of the two alcohols in fermentation liquors.

THE partition method (*3–7*) for the determination of fatty acids in a mixture may be applied to the determination of ethyl and butyl alcohols in a mixture with good results. The procedure is simple, rapid, and accurate. The alcohols are oxidized to fatty acids with potassium dichromate in the presence of orthophosphoric acid. The acids are distilled and the distillate partitioned between isopropyl ether and water as described in the partition method. From a calculation of the percentage of acid distributed to the aqueous phase, the percentages of each of ethyl and butyl alcohols can be read directly from the nomogram in Figure 2. This method is especially useful in the quantitative determination of ethyl and butyl alcohols in fermentation liquors when either one or both are present.

Van der Lek (*1*) has determined these alcohols by oxidizing with dichromate and sulfuric acid, steam-distilling the volatile acids, and then determining the acids by the method of Duclaux.

Procedure

The alcohols are distilled from the neutral fermentation medium by direct distillation. Should substances such as acetaldehyde, acetoin, or acetone be present in the distillate to interfere with the final results due to oxidation to acetic acid, they should be removed by precipitation with some suitable substance such as 2,4-dinitrophenylhydrazine as prepared by van Niel (*2*).

For the oxidation, 50 cc. of the alcoholic distillate are placed in a 200-cc. balloon flask containing 10 grams of C. P. potassium dichromate and 25 cc. of 85 per cent phosphoric acid (ortho). The flask must be fitted with an efficient reflux condenser, preferably with a spiral condensing tube. A few pieces of porcelain are added to prevent bumping, and the mixture heated at such a rate that it boils in 1.5 minutes. Gentle boiling is then continued for 3 minutes. The condenser tube is washed down two or three times during the boiling with 5-cc. portions of water. If the process is carefully carried out and if the condenser is efficient, no volatile constituents will be lost. The flask is cooled rapidly by immersing it, with the condenser still attached, in cold water. As soon as the flask is cooled to avoid loss of volatile acid, the condenser is again washed down with 15 cc. of water. The flask is removed and connected to a Liebig condenser, and the mixture distilled until it begins to foam. There is no tendency to bump, and distillation proceeds smoothly. When the foam

[1] Received March 9, 1931.

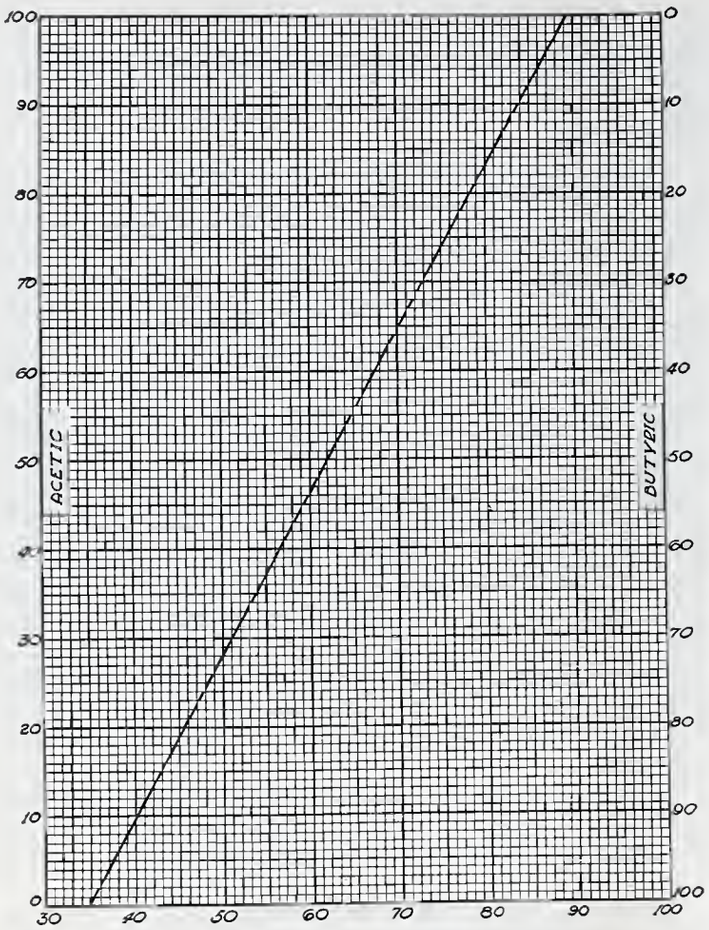


Figure 1—Partition of Acetic and Butyric Acids between Isopropyl Ether and Water

Ordinates indicate per cent of each acid present; abscissas, per cent of acid in aqueous phase (K_1)

which forms has risen to half the volume of the flask, heating is reduced until foaming is just maintained. If the heating is then continued for about 3 minutes, all of the organic acids but none of the phosphoric acid are distilled over. The distillate should be colorless and about 85 cc. in volume. This volume is made up to 100 cc. with distilled water.

Ethyl alcohol is oxidized completely to acetic acid; butyl alcohol, due to β-oxidation, gives a mixture of butyric and acetic acids containing 90.3 per cent of butyric acid and 9.7 per cent of acetic. No formic or propionic acid is present. In order to establish this constant for butyl alcohol, several solutions were oxidized containing from 50 to 600 mg. of butyl alcohol in the 50-cc. volume used for analysis. The constants obtained were: 90.0, 90.2, 90.0, 90.5, and 91.0 per cent butyric acid.

The butyl alcohol was purified by repeated fractionation through a Young fractionating column. The middle fraction of the distillate was collected each time until a fraction with a constant boiling point of 117° C. was obtained. This fraction was further redistilled until a constant oxidation factor was obtained.

Thirty cubic centimeters of the acid solution, approximately 0.1 N, are shaken for 1 minute in a separatory funnel with 20 cc. of isopropyl ether at 25° C. After 3 minutes, 25 cc. of the water layer are withdrawn and titrated with 0.1 N sodium hydroxide. The cubic centimeters of sodium hydroxide required are recorded as P'. Twenty-five cubic centimeters of the original acid solution are titrated and the number of cubic centimeters of sodium hydroxide is recorded as M. Then $P'/M \times 100 = K$. This K is designated as the percentage partition constant for the acid solution. These percentage partition constants have the same significance as the constants employed by Osburn and Werkman (*3*), but in this case the acid need not be adjusted to exactly 0.1 N.

In Figure 1, the values of K are plotted against the percentages of the acids. It is thus possible to read off the per cent of each acid from any determined value of K. If pure acetic acid is present, the value of K will be 89.0. If only butyric acid is present, the value of K will be 34.8. Mixtures of the acids give intermediate values of K. From Figure 1 the per cent of each acid can be obtained. The per cent of each alcohol can then be calculated since 1 cc. of molar alcohol, regardless of which one, gives 1 cc. of normal acid.

It is more convenient to construct a diagram from which the per cent of each alcohol may be read directly.

Since pure butyl alcohol gives on oxidation 90.3 per cent butyric and 9.7 per cent acetic acid, it is evident from Figure 1 that pure butyl alcohol would give on oxidation and partition a value of $K = 40$. If pure ethyl alcohol is oxidized, then $K = 89$. In Figure 2 the values of K between 40, representing 100 per cent butyl alcohol, and 89, representing 100 per cent ethyl alcohol, are plotted against the percentages of the alcohols.

An example will make clear the use of Figure 2. An unknown mixture of ethyl and butyl alcohols gives on oxidation and partition a value of $K = 70.5$. From Figure 2 it is seen that if $K = 70.5$, the alcohol in the mixture must be 62 per cent ethyl and 38 per cent butyl. The number of cubic centimeters of 1.0 M alcohol in the 50 cc. taken must be the same as the number of cubic centimeters of 1.0 N acid produced. Since the total acid produced is known, it is a simple matter to calculate the weights of each alcohol present.

Discussion

The method as described is accurate for solutions which give approximately 0.1 N acid when the distillate is made up to 100 cc.

The percentage partition constants for the acids shift somewhat as the acid solutions become more dilute. The method holds quite well down to about 0.05 N. If it is necessary to work with more dilute acids, new constants should be established to fit the conditions.

The procedure as outlined should be followed in detail

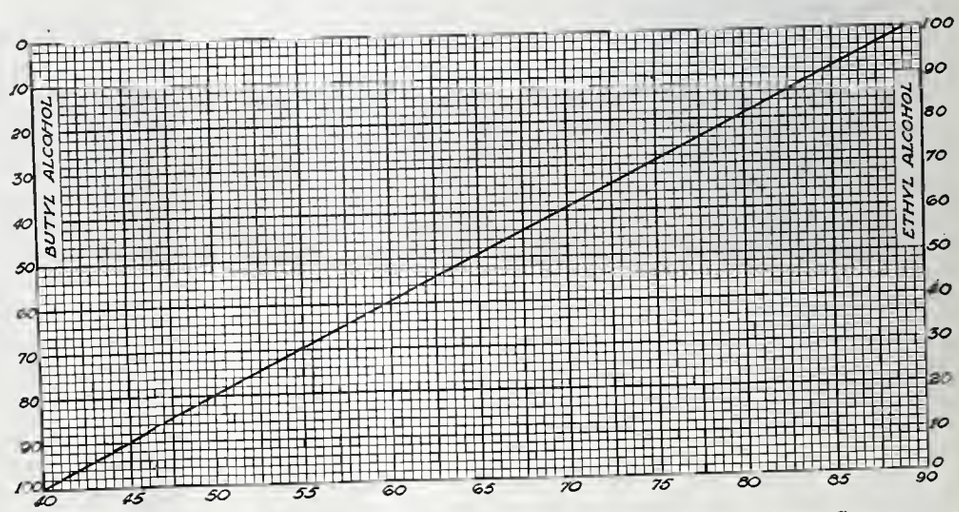


Figure 2—Per Cent of Butyl and Ethyl Alcohols from Percentage Partition Constants of Corresponding Acids

Abscissas indicate percentage partition constants (K)

since changing the concentration of the oxidizing constituents causes considerable change in the ratio of acetic to butyric acid. The manner of heating the mixture may also cause a slight variation in the acid ratio. This is in substantial agreement with the results obtained by van der Lek (*1*).

If isopropyl alcohol is present, it will be oxidized to acetone. The oxidation does not stop at acetone but goes on to acetic acid. (The formic acid produced is oxidized to carbon dioxide and water.) It is estimated that 5 to 10 per cent of the acetone so produced is oxidized. Small quantities of acetone do not interfere with the partition method. Isopropyl alcohol is infrequently present in fermentation liquors and then only in traces.

If acetone is produced, it can be precipitated from an aliquot with 2,4-dinitrophenylhydrazine and the isopropyl alcohol can be estimated.

If acetone is present in the original alcohol solution, it should be precipitated and filtered. The filtrate should be made alkaline with sodium hydroxide and the alcohols distilled. Characteristic analyses are reported in Table I.

Table I—Results of Analyses of Alcohol Mixtures

Alcohol Taken		Alcohol Found			Total Alcohol
Ethyl	Butyl	K	Ethyl	Butyl	
%	%	%	%	%	%
69.0	31.0	73.8	68.9	31.1	99.8
69.0	31.0	74.0	69.0	31.0	98.0
82.3	17.7	80.5	82.5	17.5	99.5
82.3	17.7	79.6	80.7	19.3	97.5
100	0	88.5	99.0	1.0	97.0
69.9	30.1	73.5	68	32	96.5
0	100	39.6	0	100	99
30	70	72.5	34	66[a]	100
0	100	39.9	0	100	100
30	70	55.2	30.2	69.8	98.8

[a] Total normality of acid produced was only 0.02.

Literature Cited

(1) Lek, van der, "Onderzoekingen over de butylalkoholgisting," Thesis, Delft, 1930.
(2) Niel, van, "The Propionic Acid Bacteria," Thesis, Delft, 1928.
(3) Osburn and Werkman, Ind. Eng. Chem., Anal. Ed., **3**, 264 (1931).
(4) Werkman, *Ibid.*, **2**, 302 (1930).
(5) Werkman, *Iowa State Coll. J. Sci.*, **4**, 459 (1930).
(6) Werkman, *Ibid.*, **5**, 1 (1930).
(7) Werkman, *Ibid.*, **5**, 121 (1930).

A Low-Temperature Thermostat[1]

H. W. Foote and Gosta Akerlof

Department of Chemistry, Yale University, New Haven, Conn.

THE thermostat described below is the outcome of an attempt to use a regulated cold supply, from a small electric refrigerating unit, to maintain a constant low temperature in the same way that a regulated heat supply is used to maintain a constant high temperature. The thermostat has been in continuous use for several months and appears to run equally well at any temperature between the minimum room temperature and 0° C. It has not been tested below the latter. The variations in temperature can, if desired, be kept within ±0.015°, and the apparatus requires no more attention when running than the ordinary electrically heated thermostat.

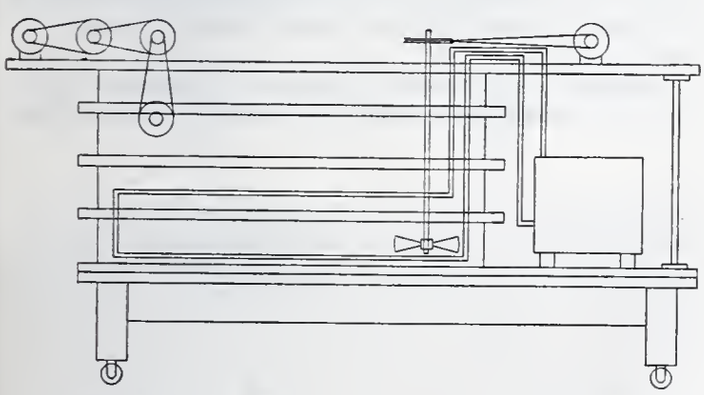


Figure 1—Diagram of Low-Temperature Thermostat

The apparatus consists essentially of a tank (Figure 1) holding about 450 liters. At one end, the cooling unit, consisting of a 1/6-horsepower motor and compressor, rests on the lower shelf. A copper tube, about 60 feet (18.28 meters) long, containing the refrigerant leads through a valve, not shown in the diagram, into the tank and is coiled around the inside on a wooden frame. The motor on the upper shelf at the right is connected with a stirring apparatus as indicated. The apparatus at the left is for solubility determinations, and when in use provides sufficient stirring so that the other stirrer is not used unless exceedingly close temperature control is required. The tank is lined with tinned copper and is heat-insulated with two layers of "insulite" between the metal and wood. Horizontal cleats run about the outside of the tank through which run upright iron rods for holding equipment. The cover is in sections so that a part of the tank can be uncovered without undue heat exchange with the surroundings.

A diagrammatic wiring plan for regulating the temperature is shown in Figure 2. At *A*, a d. c. potential of 110 volts allows a constant small current to pass through a fixed resistance of 750 ohms. From this resistance, a small current of about 5 milliamperes, which passes to the regulator *B* and activates a small relay, *C*, is tapped. This relay was not capable of carrying the current necessary for the cooling unit, and therefore a second rather heavy relay which could be used on an alternating current was used, and the cooling unit *D* was placed in the circuit as shown.

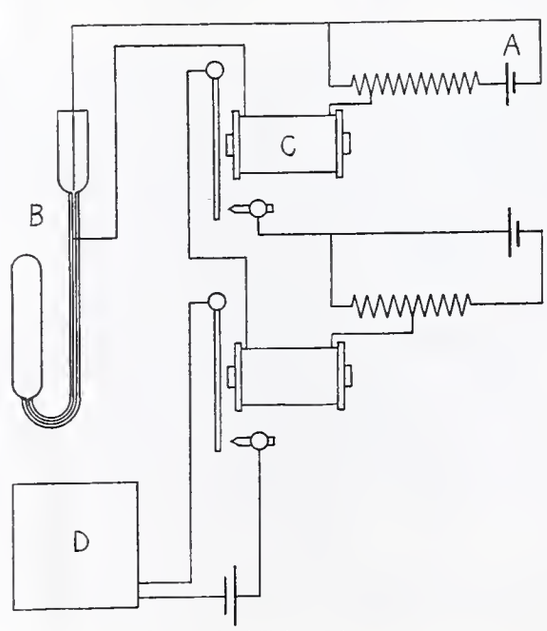


Figure 2—Wiring Diagram

[1] Received May 8, 1931.

It is evident that in general the shorter the periods of time during which the cooling unit runs or is at rest, the more constant the temperature will be. On the other hand, the longer the periods, the less will be the strain on the motor from starting. With very efficient stirring, it was found in test runs at 6° C. that the refrigerating unit ran for a period of about 3 minutes and was at rest for a somewhat longer period. The variation in temperature under these conditions did not exceed ±0.015° and was usually within ±0.01°. By stirring less violently, by means of the solubility apparatus, the motor ran in periods of about 7 minutes and the variation in temperature was slightly greater, possibly ±0.025°. When this variation is not objectionable, the slower stirring is preferable.

The toluene-mercury regulator was at first fastened directly to the tank. Owing to vibrations from the motor, the mercury surface was kept in constant motion, and the contact between mercury and platinum wire was continually interrupted, causing the motor to run erratically. This was corrected by fastening the regulator to a support which was not connected with the tank. The shape of the platinum tip making the connection at the mercury surface was also found important in causing the motor to start and stop promptly. A smooth, flat point was found preferable to a needle point.[2]

The special apparatus used in the construction consisted of a Kelvinator Condensing Unit L-53, a small relay running on direct current, and a larger Westinghouse relay running on alternating current.

By suitable modifications in the wiring and the use of a heating coil, the apparatus can be used for high temperatures as well as low.

The writers are particularly indebted to Professor Herbert S. Harned of this laboratory for advice and suggestions regarding the thermostat.

[2] The referee has suggested that a nickel wire might make a better contact than platinum, as the former is not wetted by mercury.

Determination of Iron in Milk and Other Biological Materials[1]

Ralph Stugart

Reed and Carnrick, Jersey City, N. J.

The iron content of milk and milk powder reported by various authorities varies widely, and this variation can be traced not so much to the contamination of the milk as to the methods of analysis employed and to the procedure in preparing the material for analysis.

The colorimetric method using ferrocyanide cannot be used in the presence of appreciable amounts of phosphorus and calcium.

The sulfocyanate method employing amyl alcohol for extracting the ferric sulfocyanate is reliable. The determination involving the comparison of aqueous solutions is not permissible owing to the fading of the color. The use of ether for extracting the iron sulfocyanate is not satisfactory and acetone does not afford a guarantee against fading. The iron content of milk cannot be determined with sufficient accuracy by gravimetric or volumetric methods.

Methods employing large quantities of potassium or sodium hydroxide are unsatisfactory for the determination of very small amounts of iron. Potassium or sodium hydroxide cannot be freed from iron by allowing a 40 per cent solution to stand several days and decanting the clear solution. Correction for the iron in the potassium and sodium hydroxide is unsatisfactory owing to the fact that the iron is not completely precipitated, and blank determinations are unreliable because of the varying proportions of iron precipitated.

Methods using small quantities of alkali are unreliable due to the presence of iron in the sodium hydroxide and to the iron dissolved from the glass during heating. The results may indicate several times as much iron as actually present.

A method in which alkali treatment is eliminated and the iron determined as ferric sulfocyanate is given in detail.

The accurate determination of iron in milk has acquired greater importance on account of the recent work on nutritional anemia. As reported in the literature, the iron content of milk varies widely, but in an excellent review of the subject, Nottbohm and Weisswange (*21*) point out that this variation should be attributed less to the milk itself than to the inaccuracy of the method of analysis. This statement seems to apply also to the more recent data.

Herapath (*9*) was the first to take advantage of the color of ferric sulfocyanate for the determination of small amounts of iron. Later, Thompson (*26*) used the same method with slightly different procedure and the method is frequently referred to as Thompson's method. Zega (*27*) used sulfocyanate for the determination of iron in water and stated that hydrochloric acid was not so good as nitric acid for acidifying. Mai (*15*) and Soxhlet (*23*) employed this method in determining iron in milk. Andrews (*1*) found that solutions in ethyl ether, amyl alcohol, and absolute ethyl alcohol were more intensely colored than aqueous solutions, indicating that dissociation or hydrolysis was responsible for the lighter color and the fading of aqueous solutions. Moore (*18*) noted that potassium sulfocyanate could not be used as a qualitative test for iron in the presence of phosphoric acid.

In the determination of iron in milk, Ewers (*6*) found it necessary to remove the phosphates from the milk ash, and also observed that sulfocyanate could not be used in the presence of pyrophosphates. Elvehjem and Hart (*5*) removed the interfering phosphates from milk ash but made no attempt to overcome the error due to fading in aqueous solutions.

Ether was first used by Natanson (*19*) to make the test for iron with sulfocyanate more sensitive. Tatlock (*25*) used ether as a solvent for ferric sulfocyanate in the determination of iron in alum. Von Kéler and Lunge (*10*) used the procedure of Tatlock and pointed out that the determination involving the comparison of aqueous solutions was not permissible, owing to the fading of the color. Lachs and Fried-

[1] Received April 15, 1930. Presented before the Division of Medicinal Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

enthal (*13*) determined the iron in milk by a method similar to that of Tatlock. Marriott and Wolf (*16*) used acetone to reduce the dissociation of the ferric sulfocyanate, and this method has been used by several recent investigators.

Stokes and Cain (*24*) pointed out the disadvantages of ether and acetone and suggested the use of amyl alcohol or a mixture of ether and amyl alcohol. Kugelmass (*12*), Kennedy (*11*), and Elvehjem (*4*) also used amyl alcohol.

For the determination of iron in milk, Fendler, Frank, and Stüber (*7*) employed titration with potassium permanganate, and Glikin (*8*), Langstein (*14*), and Edelstein and Czonka (*3*) used iodometric methods. The iron content of milk cannot be determined with sufficient accuracy by gravimetric or volumetric methods. The errors inherent in such methods are discussed by Nottbohm and Weisswange (*21*).

Among the recent methods for the determination of iron in biological materials are those of Elvehjem and Hart (*5*), Kennedy (*11*), and Elvehjem (*4*). In the method proposed by Elvehjem and Hart, the phosphorus is removed as ammonium phosphomolybdate, and the iron present in the filtrate is precipitated by addition of a 40 per cent potassium hydroxide solution which is freed from iron by allowing to stand several days and decanting the clear solution. An attempt was made to employ this method in these laboratories early in 1929 in connection with studies on anemia, but as high and variable results were always obtained, it was obvious that iron was introduced somewhere in the procedure as an impurity. Accordingly, the 40 per cent potassium hydroxide solution was examined for its iron content and appreciable quantities were found. It was also observed that a small amount of a gelatinous precipitate was present in the solutions after boiling with 40 per cent potassium hydroxide solution, due to the action of the alkali on the glass. This action of the hot alkali on the glass vessel was another possible source of iron contamination.

In Table I will be found an analysis of nine samples of C. P. potassium hydroxide obtained from five leading chemical houses. The results represent the average of duplicate analyses of the clear solution after allowing a 40 per cent solution to stand three weeks.

Table I—Iron in 40 Per Cent Potassium Hydroxide Solution

Sample	Iron
	Mg./100 cc.
1	0.157
2	0.109
3	0.102
4	0.235
5	0.400
6	0.207
7	0.122
8	0.093
9	0.060

Several determinations were made by the Elvehjem and Hart method using 5 grams of milk powder for analysis and 50 cc. of 40 per cent potassium hydroxide solution containing 0.16 mg. of iron per 100 cc. The amount of iron introduced by the potassium hydroxide solution, therefore, amounted to 16 mg. per kilo, or about three times the amount present in the milk powder. When corrected for the amount of iron in the potassium hydroxide solution, the results were variable, because the iron was not completely precipitated. Blank determinations cannot be relied upon, owing to the varying proportions of iron precipitated. The results of several blank determinations using 50 cc. of 40 per cent potassium hydroxide solution, with different amounts of calcium nitrate to act as a "collector" for the ferric hydroxide, are shown in Table II. This method is thus seen to be unreliable for the determination of very small amounts of iron.

Kennedy (*11*) used amyl alcohol to extract ferric sulfocyanate. He prepared the material for analysis by oxidation with sulfuric acid and perchloric acid. This method of ashing is not applicable to milk.

Table II—Recovery of Iron in 40 Per Cent Potassium Hydroxide Solutions

Calcium Nitrate Added, 10% Soln.	Iron in KOH Soln.	Iron Recovered	
Cc.	*Mg./100 cc.*	*Mg./100 cc.*	*%*
None	0.060	0.014	23.3
1.0	0.060	0.037	61.6
2.5	0.060	0.047	78.3
2.5	0.160	0.133	83.1
None	0.235	0.036	15.3
2.0	0.235	0.072	30.6

Elvehjem (*4*) later pointed out that as pyrophosphate interferes with the color development in the sulfocyanate method, low results are obtained on milk and milk powder when the procedure of dry ashing is used. In order to overcome this difficulty, Elvehjem made the solution distinctly alkaline with sodium hydroxide and boiled for one hour to hydrolyze the pyrophosphate. The solution was then made acid with hydrochloric acid, potassium sulfocyanate added, and the ferric sulfocyanate extracted with amyl alcohol. In this way high results were again obtained, owing to the presence of iron in the sodium hydroxide and to the iron dissolved from the glass. If the boiling is carried out in platinum and correction made for the iron in the sodium hydroxide, the results are practically identical with the proposed method where acid hydrolysis is used. The latter method is preferable as it is more convenient, can be carried out in glass, and no correction for iron in sodium hydroxide need be made.

The amount of iron dissolved from glass by potassium and sodium hydroxide solutions varies with the kind of glass and the time of boiling. Porcelain yields more iron than glass. When using glass apparatus, fair checks can be obtained by the Elvehjem method if identical conditions are observed, but the results may indicate several times as much iron as actually present in the milk, owing to the iron derived from the glass.

In Table III data are presented to show the recovery of iron in solutions containing pyrophosphate, after acid and alkali hydrolysis.

Table III—Determination of Iron in Solutions Containing Pyrophosphate

Pyrophosphate Taken	Hydrolyzing Medium		Boiling Time	Iron Introduced with NaOH	Vessel Used	Iron Added before Hydrolysis	Iron Found
Mg.	Material	*Cc.*	*Minutes*	*Mg.*		*Mg.*	*Mg.*
200	NaOH	4	60	0.0208	Platinum	0.050	0.0715
200	NaOH	3	60	0.0156	Platinum	0.050	0.0666
200	HCl	1	25	....	Pyrex	0.100	0.1000
200	HCl	5	25	....	Pyrex	0.010	0.0101
300	HCl	5	25	....	Pyrex	0.025	0.0252
200	HCl	1	30	....	Pyrex	0.050	0.0510
200	HCl	1	[a]	....	Pyrex	0.100	0.0150
200	HCl	1	[a]	....	Pyrex	0.050	0.0134

[a] Potassium sulfocyanate added immediately without heating.

The accuracy of the method using acid for hydrolysis of pyrophosphate is shown in Table IV. No difference in results was noted when iron was added before or after ashing.

The determination of small quantities of iron in organic materials relatively low in calcium and phosphorus offers no difficulties. The colorimetric method using ferrocyanide is simple and reliable if the unknown and standard solutions contain 0.05 to 0.1 mg. of iron and 0.5 to 1.5 cc. of free hydrochloric acid before development of the color. An acid concentration above this amount tends to produce fluorescence which renders color comparison difficult and results unreliable, whereas a lower concentration prevents maximum color development. Best results are obtained if the color is developed in approximately 5 or 10 cc. of the solution, followed by immediate dilution to 100 cc. In the presence of appreciable amounts of phosphorus and calcium this method cannot be used, but the sulfocyanate method proposed by Stokes and Cain (*24*), modified as outlined below, is convenient and reliable.

Modified Method

PREPARATION OF MATERIAL—The accuracy of the results depends upon the proper preparation of the material for analysis. Because of the quantity of milk required for the determination of iron, wet ashing with sulfuric or nitric acid is unsatisfactory. Perchloric acid is also undesirable in the oxidation of large amounts of organic materials, owing not only to the danger of explosion, but also to the impurities it contains even after vacuum distillation. Dry ashing has been found reliable if due precautions are taken to prevent loss and fusion of the ash.

Desiccated material is finely ground, placed in platinum dishes, dried at 110° C. to constant weight, and transferred to an electric muffle furnace. It is then allowed to carbonize very slowly in the open muffle. As carbonization proceeds, the door of the furnace is gradually closed and the contents allowed to remain overnight, with the temperature regulated so that the muffle is just below dull redness. No loss of material or fusion of the ash will occur if this procedure is followed. In the case of milk, 100 cc. are evaporated to dryness on a water bath, and the dry material is ashed as described above. The ash is taken up in just enough iron-free hydrochloric acid to effect solution, filtered, and the filtrate set aside. The residue, consisting largely of carbon, is ignited as before and taken up with a little dilute hydrochloric acid. The filtrate and washings are added to the original filtrate and made up to 50 cc. in a volumetric flask.

METHOD—The details of the method are as follows:

IRON-FREE HYDROCHLORIC ACID—All hydrochloric acid used should be freed from iron by distillation.

STANDARD IRON SOLUTION—Weigh accurately 0.5 gram of pure iron wire and dissolve in 20 per cent hydrochloric acid with the aid of 1 cc. of concentrated nitric acid. Carefully evaporate to dryness and dissolve the ferric chloride in hydrochloric acid, avoiding large excess. Dilute to 100 cc. and preserve carefully. Each cubic centimeter of this stock solution is equivalent to 5 mg. of iron. For a working standard, take 1 cc. of this stock solution and dilute to 100 cc., then each cubic centimeter is equivalent to 0.05 mg. of iron. It is convenient to make up two standards containing 0.01 and 0.02 mg. of iron.

PROCEDURE—Pipet an aliquot part of the unknown solution containing approximately 0.025 to 0.10 mg. of iron into a 150-cc. beaker. Add 5 cc. of concentrated hydrochloric acid and make up to approximately 25 cc. Hydrolyze by boiling 20 minutes, let cool, add one drop of concentrated nitric acid, and make up to 25 cc. in a volumetric flask. Transfer an aliquot portion of 10 cc. to a 30- or 50-cc. separatory funnel, and add 1 cc. of hydrochloric acid and enough 0.1 *N* potassium permanganate to produce a pink color which persists for 20 seconds (usually 1 or 2 drops are sufficient). Add 5 cc. of isoamyl alcohol accurately measured, then 5 cc. of 20 per cent potassium sulfocyanate solution. Shake vigorously for 30 seconds, allow to separate, and draw off the water. Transfer a suitable portion of the colored alcohol to the colorimeter cup, taking precautions to exclude any droplets of water, and compare with a standard prepared as follows:

Pipet 1.0 and 2.0 cc. of the working standard equivalent to 0.05 and 0.10 mg. of iron, respectively, into each of two 50-cc. volumetric flasks. Add one drop of concentrated nitric acid, 10 cc. of hydrochloric acid, then make up to volume with distilled water. Transfer 10 cc. to a 30-cc. separatory funnel, add 1 cc. of hydrochloric acid, one or two drops of 0.1 *N* potassium permanganate, and mix. Add 5 cc. of isoamyl alcohol, accurately measured, then 5 cc. of 20 per cent potassium sulfocyanate solution. Shake vigorously for 30 seconds and compare the colored alcohol with the unknown. In the amounts present in biological materials, cobalt, manganese, nickel, and zinc do not interfere with the color development. Copper, if present in appreciable quantity, should be removed.

By their earlier method, Elvehjem and Hart found milk powder to contain 0.0032 per cent iron. By his recent method, Elvehjem found milk powder to contain 0.00226 per cent iron. If the 40 per cent sodium hydroxide solution used contained 1 mg. of iron per liter, and 1 cc. were employed in hydrolyzing 3 grams of milk powder, the amount of iron introduced per kilo of milk powder through the sodium hydroxide would be 0.33 mg. If the sodium hydroxide contained 16 mg. of iron per liter, then the amount of iron introduced by using 1 cc. of sodium hydroxide would be 5.33 mg. per kilo of milk powder. The high results obtained by Elvehjem and Hart, and Elvehjem, can be traced, no doubt, to the iron introduced with the potassium or sodium hydroxides and to the action of the hot alkali on glass.

Table IV—Determination of Iron by Proposed Method

Time of Boiling	Material	Amt. of Material	Iron Added	Iron Found		Iron Recovered
Minutes		*Grams*	*Mg.*	*Mg.*	*Mg./kilo*	%
15	Milk powder A	2.0	...	0.0098	4.90	...
30	Milk powder A	2.0	...	0.0099	4.95	...
45	Milk powder A	2.0	...	0.0098	4.90	...
60	Milk powder A	2.0	...	0.0099	4.95	...
15	Milk powder A	1.0	0.02	0.0249	4.90	99.9
20	Milk powder A	1.0	0.03	0.0347	4.70	99.3
15	Milk powder B	2.0	...	0.0098	4.90	...
15	Milk powder B	2.0	0.008	0.0177	4.85	99.4
15	Milk powder C	4.0	...	0.0192	4.80	...
30	Milk powder D	2.5	...	0.0125	5.00	...
20	Milk powder D	3.6	...	0.0179	4.97	...
20	Milk powder D	3.6	0.01	0.0279	4.97	99.8
15	Milk powder A	1.0	0.01	0.0148	4.80	99.1
15	Milk powder A	1.0	0.01	0.0150	5.00	100.5
15	Milk powder A	1.0	0.01	0.0150	5.00	100.5
20	Certified milk E	20 cc.	...	0.0088	0.44[b]	...
20	Certified milk F	20 cc.	...	0.0093	0.46	...
20	Certified milk G	20 cc.	...	0.0106	0.53	...
20	Grade B past. milk H	10 cc.	...	0.0073	0.73	...
20	Known solution[a]		0.2232	0.2193	..	98.2
20	Known solution[a]		0.1036	0.1030	..	99.4

[a] Contained pyrophosphate, copper, zinc, manganese, cobalt, and nickel. Copper removed as copper sulfide.
[b] Mg. per liter.

In Table V is tabulated the iron content of cow's milk as reported by various authorities. The wide variations in the results obtained for the very small iron content of milk can be traced, no doubt, not so much to the contamination of the milk as to the methods of analysis employed and to the procedure in preparing the material for analysis.

Table V—Iron Content of Milk and Milk Powder Reported by Various Authorities

Iron	Method Used	Authority
Mg./liter		
	MILK	
2.45	Gravimetric	Bunge (*2*)
47.6–68.9[a]	Iodometric	Glikin (*8*)
1.0	Sulfocyanate in aqueous soln.	Mai (*15*)
2.8–8.4	Titration with $KMnO_4$	Fendler, Frank, and Stüber (*7*)
1.3	Sulfocyanate in ether soln.	Lachs and Friedenthal (*13*)
0.3–0.7 coll. in glass; 0.7–3.0 commercial milk	Iodometric	Langstein (*14*)
0.45 av. in uncontaminated milk; 1.11 av. in mixed milk	Iodometric	Edelstein and Czonka (*3*)
0.17–0.84 av. of 26 samples, 0.42	Sulfocyanate in aqueous soln.	Soxhlet (*23*)
0.91	Cupferron precipitation and sulfocyanate in aqueous soln.	Nottbohm and Weisswange (*21*)
0.21–0.91[b]	Same as above	Nottbohm and Dörr (*20*)
1.2	Sulfocyanate in amyl alcohol	Kugelmass (*12*)
3.5	Sulfocyanate in aqueous soln. after removal of phosphates	Elvehjem and Hart (*5*)
2.4, av. of 20 samples	Same as above	Petersen and Elvehjem (*22*)
0.23 coll. in glass; 1.4 market milk	.....	Matsuo (*17*)
Mg./kilo		
	MILK POWDER	
32.0	Sulfocyanate in aqueous soln. after removal of phosphates	Elvehjem and Hart (*5*)
22.6	Sulfocyanate in amyl alcohol after alkaline hydrolysis	Elvehjem (*4*)

[a] Decimal point probably misplaced. [b] Most values between 0.21 and 0.49.

A number of the results in Table V are in fair agreement, although most of the methods used were lacking in accuracy. For example, Soxhlet found an average of 0.42 mg. of iron per liter of milk. Two determinations were made on pasteur-

ized milk, with an actual iron content of 0.73 mg. per liter, by the method used by Soxhlet. The results were 0.6 mg. and 0.8 mg. per liter. Kugelmass used amyl alcohol as solvent for ferric sulfocyanate; but his results were subject to error on account of the small amount of milk taken for analysis. Ashing in a glass tube seems also to result in contamination with iron since the same milk, containing 0.73 mg. of iron per liter, gave a result of 1.3 mg. by the method of Kugelmass.

Acknowledgment

The writer wishes to express his indebtedness to Frank R. Eldred for his suggestions and criticism in the course of this work, and to E. Passamaneck for carrying out many of the iron determinations.

Literature Cited

(1) Andrews, *Chem. News*, **70**, 165 (1894).
(2) Bunge, *Z. Biol.*, **10**, 295 (1874).
(3) Edelstein and Czonka, *Biochem. Z.*, **38**, 14 (1912).
(4) Elvehjem, *J. Biol. Chem.*, **86**, 463 (1930).
(5) Elvehjem and Hart, *Ibid.*, **67**, 43 (1926).
(6) Ewers, *Chem. Zentr.*, **69** (II), 605 (1898).
(7) Fendler, Frank, and Stüber, *Z. Untersuch. Nahrungs-Genussm.*, **19**, 369 (1910).
(8) Glikin, *Biochem. Z.*, **21**, 348 (1909).
(9) Herapath, *J. Chem. Soc.*, **5**, 27 (1853).
(10) Kéler, von, and Lunge, *Z. angew. Chem.*, **22**, 670 (1894).
(11) Kennedy, *J. Biol. Chem.*, **74**, 385 (1927).
(12) Kugelmass, *Bull. soc. chim. biol.*, **4**, 577 (1922).
(13) Lachs and Friedenthal, *Biochem. Z.*, **32**, 130 (1911).
(14) Langstein, *Jahrb. Kinderheilk.*, **74**, 536 (1911).
(15) Mai, *Z. Untersuch. Nahrungs-Genussm.*, **19**, 21 (1910).
(16) Marriott and Wolf, *J. Biol. Chem.*, **1**, 451 (1906).
(17) Matsuo, *Osaka J. Med.*, **28**, 555–62 (1929).
(18) Moore, *Chem. News*, **53**, 209 (1886).
(19) Natanson, *Ann.*, **130**, 246 (1864).
(20) Nottbohm and Dörr, *Z. Untersuch. Nahrungs-Genussm.*, **28**, 417 (1914).
(21) Nottbohm and Weisswange, *Ibid.*, **23**, 514 (1912).
(22) Petersen and Elvehjem, *J. Biol. Chem.*, **78**, 215 (1928).
(23) Soxhlet, *Münch. med. Wochschr.*, **59**, 1529 (1912).
(24) Stokes and Cain, *J. Am. Chem. Soc.*, **29**, 409 (1907).
(25) Tatlock, *J. Soc. Chem. Ind.*, **6**, 276 (1887).
(26) Thompson, *J. Chem. Soc.*, **47**, 495 (1885).
(27) Zega, *Chem.-Ztg.*, **85**, 1564 (1893).

The Buffer Capacity of Sea Water[1]

Thomas G. Thompson and Robert U. Bonnar

Department of Chemistry and Oceanographic Laboratories, University of Washington, Seattle, Wash.

The buffer capacity of sea water is defined and the principle of the determination demonstrated. The buffer capacity is differentiated from such terms as "alkaline reserve," "methyl orange alkalinity," etc., because the effects upon the indicator by variations in the concentration of the dissolved salts and of the excess acid are considered.

The buffer capacity is shown to be a rather constant function of normal sea waters, and the value of the constant for the Puget Sound region and the San Juan Archipelago shown to be 0.1250 with chlorinity per liter as unity. However, variations in conditions affecting the sea water, such as land drainage, pollution, and photosynthesis, cause noticeable deviations.

The total carbon dioxide cannot be determined by direct acidimetric titration methods. Sea water diluted by streams tends to give a high value for the buffer capacity. Photosynthetic processes and industrial pollution of sulfite liquor give low buffer-capacity values.

The determination is one that may be easily and quickly performed under rigorous field conditions.

The buffer capacity of sea water may be defined as the number of millimoles of hydrogen ions which a unit volume of sea water will neutralize when an excess of standard acid is added. The principle of the method is to add a measured quantity of standard acid to a known amount of freshly sampled sea water, determine the hydrogen-ion concentration of the resultant solution, using special standards for comparison, and calculate the amount of acid neutralized.

The buffer capacity is in the category of the "alkalinity" of Ruppin as cited by Helland-Hansen (*1*). It is analogous to the "alkaline reserve" of McClendon (*3*) because no difference was noted in the buffer capacity when the sea water was boiled, either before or after the addition of the acid. It is also similar to the "titrable alkalinity as bicarbonate" of Lucas and Hutchinson (*2*), if certain corrections are made for the end points. However, the use of the term distinguishes it from others that are analogous because recognition is made of the effects produced by varying the concentration of dissolved salts and the excess of acid. The present paper is an extension and improvement of previous work reported from the authors' laboratories (*5*).

Variations in the concentration of the dissolved salts occurring in sea water have variable "salt effects" upon the indicators. Thus in the determination of the buffer capacity, certain corrections must necessarily be applied. This is best accomplished by the use of what is termed "base-free" sea water. Colorimetric standards may be prepared by adding varying known quantities of acid to the base-free sea water, the latter being first diluted to a salt content equivalent to the waters being studied.

[1] Received May 22, 1931.

Preparation of Base-Free Sea Water

Four liters of sea water are boiled with a small excess of sulfuric acid. Three or four drops of the concentrated acid are sufficient. After thorough boiling, 0.01 *N* sodium hydroxide is added until a pH of 6.6 is obtained, using bromothymol blue and La Motte standards. The sea water is again boiled, cooled, and the chlorinity (*6*) determined.

Knowing the latter and the chlorinities of the samples of sea water to be studied, the base-free sea water is diluted with distilled water until analogous conditions of concentration are obtained. The base-free sea water is used for the preparation of standards within the range of bromophenol blue by the addition of carefully measured amounts of standard 0.0100 *N* hydrochloric acid. It is necessary to prepare different sets of standards of the varying quantities of acid for different ranges of chlorinity. In practice it is found more convenient to restandardize by comparison with the La Motte color standards. Bromophenol blue is used because it is not sensitive to the hydrogen ions of the carbonic acid formed, and thus the boiling of the solution is not necessary.

The method for the determination of the buffer capacity has been subjected to four modifications. The first, applicable to waters having chlorinities between 14.50 ‰ and 18.00 ‰, was to add 25.00 ml. of 0.0100 *N* hydrochloric acid to 100 ml. of sea water and then take the pH of the resultant solution,

using bromophenol blue as the indicator and standards of base-free sea water of a given chlorinity for comparison. This method, because of its rapidity, has proved particularly useful aboard ship and under the most rigid conditions, as a large number of bottles containing the necessary amount of acid may be prepared in advance.

The second modification consisted in varying the concentration of the acid for waters of lesser or greater chlorinities so that the excess acid would come within the proper range of the bromophenol blue.

The third modification was to titrate with 0.01 N hydrochloric acid to a color approximately in the middle of the range of bromophenol blue and to determine the pH of the resultant solution in the usual manner.

The fourth modification might be termed a micro-method as a 10-ml. sample was measured into a calibrated pH tube, titrated with the standard acid with a microburet, and the pH noted.

It is essential that the 0.0100 N hydrochloric acid be prepared by dilution with distilled water from 0.1000 N hydrochloric acid in order to minimize titration errors.

The computations to be considered in the determination of the buffer capacity of sea water are the calculations of the amount of acid added and the calculations of the concentration of the resultant acid, using the standards prepared from base-free sea water. For convenience, results are reported as millimoles per liter of sea water, and may be calculated from the following formula:

$$Bc = \left[\left(\frac{1000}{Vs}\right)(V)(N)\right] - \left[\frac{1000\,(Vs + V)Hs}{Vs}\right] \qquad (1)$$

where Bc is the buffer capacity; Vs is the volume of sea water used; V, the volume of acid in milliliters; and N, the normality of the acid. The first part of the expression is the millimoles of hydrogen ions added per liter of sea water, while the second part of the expression is the millimoles of hydrogen ions in excess. The latter is found by determining the pH, which is designated as pHs because of correction for salt effects, where

$$\mathrm{pH}s = \log \frac{1}{[Hs]} \qquad (2)$$

Hs may be determined for any given series of determinations for the chlorinity range under consideration and for the nature and the concentration of the indicator utilized, as follows:

$$Hs = \frac{(V_1).(N)}{(Vb + V_1)} \qquad (3)$$

where Vb is the volume of base-free sea water, and V_1, the volume of the acid added to the base-free sea water in the preparation of the color standards.

It is obvious that the buffer capacity is practically independent of the original pH of the sea water under consideration.

Illustration—A sample of sea water had a chlorinity of 17.95 grams per liter. A 100-ml. portion of this water was added to 25 ml. of 0.0100 N hydrochloric acid and a quantity of the resulting solution measured in a pH tube. Bromophenol blue indicator was added and the color produced compared with standards made from base-free sea water of approximately the same chlorinity. A match with the color standards showed a pHs of 3.8. This particular standard had been made by adding 1.50 ml. of 0.0100 N hydrochloric acid to 100 ml. of base-free sea water. Thus

$$3.8 = \log \frac{1}{Hs}$$

$$Hs = 0.00015$$

or, substituting in Equation 3,

$$Hs = \frac{1.5 \times 0.01}{100 + 1.5} = 0.00015$$

Then applying Equation 1

$$Bc = \left[\frac{1000}{100} \times 25 \times 0.01\right] - \left[\frac{1000\,(100 + 25)\,0.00015}{100}\right] = 2.31$$

Experimental Procedure

The data presented in Table I emphasize the errors that may be produced by dissolved salts and variations of excess acid. In order to get concordant and comparable results, it is necessary to use sufficient hydrochloric acid in excess to give a color reading equivalent to a pH between 3.7 and 4.4, and to standardize color-comparison tubes in terms of a base-free sea water.

Table I—Variations in Acidity with Bromophenol Blue
(100 ml. of base-free sea water; chlorinity, 15‰)

0.01 N HCl Added	Concentration of Resulting Solution		
	Calcd. H^+	Obsd. H^+	Diff.
Ml.			
1.00	0.099	0.028	0.071
2.00	0.196	0.063	0.133
3.00	0.291	0.100	0.191
4.00	0.384	0.140	0.270
5.00	0.476	0.200	0.276

From August, 1928, to March, 1930, 452 samples, taken at different depths from various parts of the San Juan Archipelago and the Puget Sound region, were studied. Of these samples, 130 gave abnormal values of buffer capacity because of land drainage or industrial pollution. The remaining 322 will serve for the development of the behavior of standard sea water.

The effect of silicates cannot be ignored, as the waters of the Puget Sound region contain at least 0.05 milliequivalent. The concentration of borates is unknown. On the other hand, the total effect of phosphates and hydroxyl ions is less than 0.01 milliequivalent. Likewise, ammonia, in the quantities usually present, is negligible. The carbonates and the bicarbonates are the predominating ions affecting the buffer capacity of sea water, but from a study of the data given, the authors are of the opinion that the buffer capacity is also a function of some inherent basic property of the sea.

The usual standard of comparison for sea-water behavior is the chlorinity (grams of halide as chloride) per liter or per kilo (*4*, *7*). Thus the first step is to find the ratio of the buffer capacity to chlorinity. The 322 samples gave an average ratio of 0.1252—that is

$$\frac{Bc}{Cl} = 0.1252$$

The average of the deviations of the individual samples was determined from this average ratio. A statistical method was then applied, and it was found that 283 samples, or 88 per cent of the total number, whose deviations were not more than twice the average deviation, gave an average ratio of 0.1251. Applying this method again to the 283 samples, it was found that 254, or 79 per cent of the 322, gave an average ratio of 0.1250. This figure may thus be taken as the buffer capacity–chlorinity ratio for the waters of the Puget Sound region and the San Juan Archipelago, and those ocean waters of the Northeast Pacific which serve as sources of waters for these regions. In other words, the buffer capacity expressed as millimoles is one-eighth of the chlorinity and is practically constant for waters in which the equilibria have not been subjected to any marked stress.

The next step is to multiply the difference between the standard ratio and the ratio for a given sample of water having an abnormal buffer capacity, by the chlorinity of the sample. This gives the actual deviation of the buffer capacity, in millimoles, from normal behavior. It was found that 162 samples, or 50 per cent of the 322 samples, agree with

the ratio to within the error of the determination, ±0.04 *Bc*, while 48, or 15 per cent, have a deviation just equal to the difference between the normal and the next adjacent value. Unmistakable deviations were shown by the other 112 samples, or 35 per cent of the total.

Table II—Distribution of Deviations of Buffer Capacity with Depth

	1–5 Meters	6–10 Meters	11–25 Meters	26–50 Meters	Over 50 Meters	Total
Number of samples	111	51	66	45	49	322
Number deviations	45	18	24	11	14	112
Per cent deviations	41	35	36	24	29	35
Increments:						
Number	30	12	13	4	6	65
Per cent deviations	67	67	54	36	44	59
Average deviations	0.07	0.07	0.07	0.06	0.05	0.06
Maximum deviations	0.17	0.13	0.14	0.08	0.06	
Decrements:						
Number	15	6	11	7	8	47
Per cent deviation	33	33	46	64	56	41
Average deviation	0.08	0.06	0.07	0.05	0.05	0.06
Maximum deviation	0.14	0.09	0.12	0.07	0.07	

The distribution of deviations from the normal buffer capacity is summarized and shown in Table II.

The data show that the greatest deviations are in the waters between the surface and depths of 25 meters. Abnormally high values occur more often than low values in these surface layers. The samples that deviated from the normal in the deeper samples showed greater tendency to give lower values.

Factors producing deviations in the buffer capacity are land drainage, effects of biological phenomena, and industrial pollution. In all cases of land drainage, high values for the ratio have been obtained. Photosynthetic action may be such as to give low ratios, whereas industrial pollution, such as discharge from sulfite paper mill, will give very low values for the ratio.

Table III—Data Illustrating Definite Buffer-Capacity Behavior Found in Estuaries of Puget Sound

Source of Samples	Chlorinity *Grams/liter*	Buffer Capacity *Millimoles*	*Bc/Cl*	Devn., *Bc* *Mm./liter*	Carbon Dioxide *Millimoles*	Oxygen *Mg./liter*	pH
LAND DRAINAGE							
Oyster beds near mouth of stream:							
High tide	13.08	1.84	0.141	0.20	1.86	5.90	7.70
Low tide	10.30	1.47	0.143	0.14	1.36	13.40	7.95
PHOTOSYNTHESIS							
Oyster beds in lagoon:							
Low tide 1	14.72	1.55	0.105	−0.29	1.07	21.53	Over 8.8
Low tide 2	14.75	1.62	0.110	−0.22	1.38	24.67	Over 8.8
SULFITE LIQUOR							
Near mill	5.91	0.46	0.078	−0.28	..	0.00	Less than 6.0
COMBINED EFFECTS							
Photosynthesis, land drainage, and sulfite liquor	12.31	1.03	0.084	−0.51	1.75	6.69	7.45

Many investigators have shown that photosynthesis is always accompanied by an increase in the pH of the waters, a decrease in the total carbon dioxide content, and an increase in dissolved oxygen. Sulfite liquor has a tendency to lower the pH and the dissolved oxygen, and increase the total carbon dioxide. In the latter case, the buffer capacity generally will be considerably lower than the effect produced by marked conditions of photosynthesis. In complex situations where there is much photosynthesis occurring in the sea water polluted by sulfite liquor, the pH and the dissolved oxygen may vary considerably, the total carbon dioxide will be greater than with waters subjected only to photosynthetic action, and the buffer capacity will be low. The data in Table III illustrate the effects produced.

From these data three conclusions may be drawn: (1) The buffer capacity may be only partially dependent upon the concentration of carbonates and bicarbonates; (2) the formulation of McClendon, correlating pH, carbon dioxide, and alkali reserve, lacks universal application; and (3) the determination of total carbon dioxide by titration and colorimetric methods is not feasible.

All values for total carbon dioxide reported herein were obtained by boiling off the gas after acidifying the sea water and collecting the gas in standard barium hydroxide solutions.

In order to show the contrasts between various methods for the determination of alkalinity, carbon dioxide, and buffer capacity, six different samples of sea water were collected in the San Juan Archipelago and analyzed. The data obtained are given in Table IV.

Table IV—Comparison of Methods for Determination of Alkalinity, Carbon Dioxide, and Buffer Capacity, with Related Data on Surface Waters of Washington Sound

	1	2	3	4	5	6
Chlorinity, grams per liter	16.83	16.71	16.93	17.01	16.23	15.10
Temperature, ° C.	8.1	8.2	8.2	8.3	8.7	8.8
pH	7.95	8.10	7.90	7.85	7.80	7.85
Dissolved oxygen, mg. per liter	10.08	10.68	9.24	8.92	9.36	9.16
Total carbon dioxide, millimoles per liter	1.82	1.86	1.82	1.94	1.80	1.69
Buffer capacity,[a] millimoles H^+ per liter	1.85	1.95	1.99	1.95	1.91	1.73
Buffer value per chlorinity, *Bc/Cl*	0.110	0.117	0.118	0.115	0.118	0.115
Deviation of buffer capacity	−0.25	−0.14	−0.13	−0.18	−0.12	−0.16
Alkalinity, millimoles:						
With methyl red	1.82	1.84	1.92	1.89	1.84	1.74
With methyl orange	1.99	1.95	2.01	1.97	1.89	1.80
With bromophenol blue (cold)	2.23	2.24	2.24	2.25	2.13	1.99
With bromophenol blue (hot)	2.65	2.48	2.72	2.62	2.56	2.25

[a] Boiled before and after with various samples and same results obtained as on fresh samples.

The high oxygen content indicates processes of photosynthesis, and a low *Bc/Cl* might thus be predicted. The alkalinity was determined by titration, using different indicators. The data under alkalinity show that in some cases methyl red may give a fair indication of the total carbon dioxide, but noticeable variations may be obtained. With methyl orange as the indicator, the results are higher, and bromophenol blue gives still higher results. In all the data reported, duplicate and ofttimes triplicate determinations were run on the samples. In all the alkalinity determinations the greatest variation on the same sample was 0.03 millimole. For values obtained by titration no corrections were made for the salt errors of the indicators.

To insure concordant results in the alkalinity determinations, boiling of the solutions was essential. This process is very inconvenient aboard ship, and as the buffer capacity does not show any variation whether or not the samples are heated to boiling, it thus serves as an excellent means for arriving at values that lend themselves readily to interpretation. Comparison of the titrable values with bromophenol blue and the buffer capacity emphasize the differences that may be produced by excess acid.

Neither the buffer capacity nor the titration values show a constant and concordant relationship with the total carbon dioxide nor with the dissolved oxygen.

Literature Cited

(1) Helland-Hansen, *Intern. Rev. Hydrograph*, **11**, 401–406 (1923).
(2) Lucas and Hutchinson, *Trans. Roy. Soc. Can.*, [3], **V21**, 486–496 (1927).
(3) McClendon, *J. Biol. Chem.*, **30**, 265–288 (1917).
(4) Thompson, Lang, and Anderson, *Pub. Puget Sound Biol. Sta.*, **5**, 277–292 (1927).
(5) Thompson, Miller, et al., *Pub. Puget Sound Biol. Sta.*, **7**, 67 (1929).
(6) Thompson and Van Cleve, *Rept. Intern. Fish. Com.*, No. **3**, 1–14 (1930).
(7) Thompson and Wright, *J. Am. Chem. Soc.*, **52**, 915–921 (1930).

Studies in Adiabatic Calorimetry[1]

S. W. Parr and W. D. Staley

Burgess-Parr Company, Moline, Ill.

IN THE Power Test Codes of the American Society of Mechanical Engineers for instruments and apparatus now approaching their final form, Part 9 for the Heat of Combustion says, in paragraph 14:

> An effective method of minimizing cooling errors consists in accurately controlling the temperature of the calorimeter environment. This is done by providing a complete water jacket, the temperature of which is kept constant to two or three hundredths of a degree by means of a sensitive thermostat,* * * * * * but no commercial instrument of this type is at present available.

The directions then proceed on the theory that a water-jacketed instrument is available and directions are elaborated for applying a correction factor for radiation. This matter of deriving the radiation correction in single-unit instruments

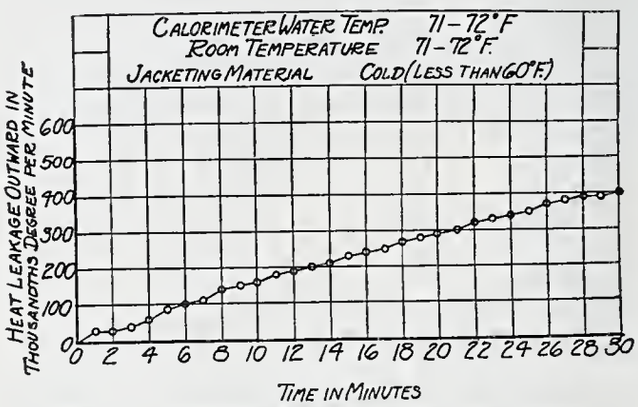


Figure 1—Radiation Loss Due to High Heat Head

is cumbersome, requires the close attention of the operator, and at best is susceptible of errors that it would be highly desirable to avoid. It is useless to hold up the ideal of a water-jacketed instrument thermostatically controlled and having such a constant radiation rate that the correction may be read from a chart if, as seems to be the case, only two such instruments are in existence. The Code acknowledges two, one at the Bureau of Standards, and one in use by the Bureau of Mines. With a water-jacket mass

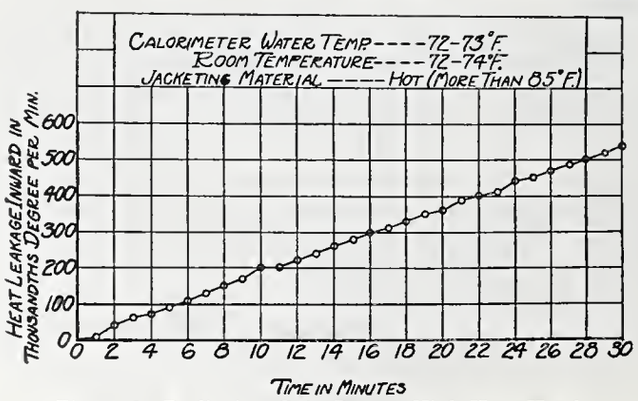


Figure 2—Radiation Gain Due to High Heat Head

of something like a thousand gallons, it is obvious that these conditions can easily be maintained. It is obvious also that the production of a unit for individual use by a manufacturer observing these conditions is beset with difficulties, and the Code says no such instruments are available.

The attempt to obviate these difficulties is the most natural thing to expect and it is believed that further progress is indicated by the experiments recorded in this paper. The most natural thing to undertake would be the avoidance of radiation factors by securing adiabatic conditions, and in this direction of effort, the most natural line of procedure would be to utilize the insulating properties of a vacuum jacket. For some reason, instruments of this type have not met with very hearty endorsement. The statement usually accompanying a discussion of this feature is that the idea is good but the practice bad.

White (*2*) states that "the sources of error and the inconvenience which characterizes the vacuum-walled calorimeter are clearly serious only in work of high precision, hence its most unqualified success has been in work of low precision." It is obvious that a manufacturer of calorimeters would not like to advertise his ware as adapted to work of low precision.

Other experimenters have found this adiabatic type of insulation erratic and uncertain and have abandoned the attempt at its utilization. Stansfield and Sutherland (*1*) list three reasons for discontinuing the use of a vacuum cup calorimeter: (1) The vacuum cups were subject to collapse; (2) the water equivalent of the calorimeter apparently changed; and (3) there was a change in the rate of cooling per minute per degree rise in calorimeter temperature. The exact reasons for the results were not definitely determined.

This situation seemed to present an opportunity to verify the disadvantages existing in the use of a vacuum-wall jacket in calorimeters for determining heat of combustion or to determine a means of overcoming these difficulties.

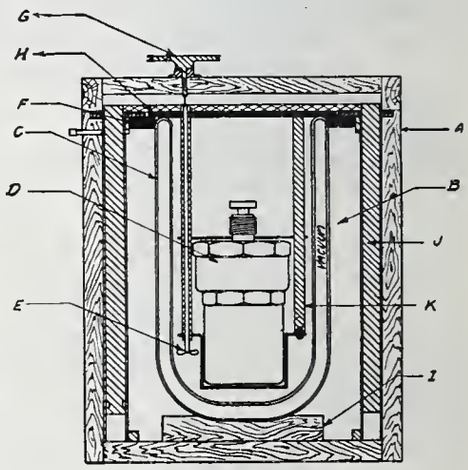


Figure 3—Type of Insulation

The first series of experiments involved the use of a vacuum vessel of 136 mm. inside diameter, 165 mm. outside diameter, and with an inside depth of 292 mm. This was mounted in a square Bakelite housing with outside dimensions of 305 mm. by 305 mm. by 375 mm. The jacket cover was constructed with a circular piece of felt on the underneath side and then a smaller disk of Bakelite which just fitted within the top of the vacuum vessel.

The temperature of the testing laboratory of the Burgess-Parr Company was allowed to drop overnight to between 50° and 60° F. (10° and 15.56° C.). Upon starting the tests in the morning, with the room at 71° F. (21.67° C.) and the calorimeter water at 71° or 72° F. (21.67° or 22.22° C.), there was marked heat leakage outward. It was suspected that with the vacuum wall, 2 or 3 inches (5.08 or

[1] Received April 11, 1931. Presented before the Division of Gas and Fuel Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

7.62 cm.) of good Balsam wool insulation, and a retaining jacket of Bakelite, there was too much or too good insulation, and a high heat head existed in the calorimeter, which accounted for the leakage outward. The Balsam wool was removed and a thermometer inserted in the air-jacketing space. Upon repeating the experiments it was found that the temperature of the air-jacketing space was low, thus

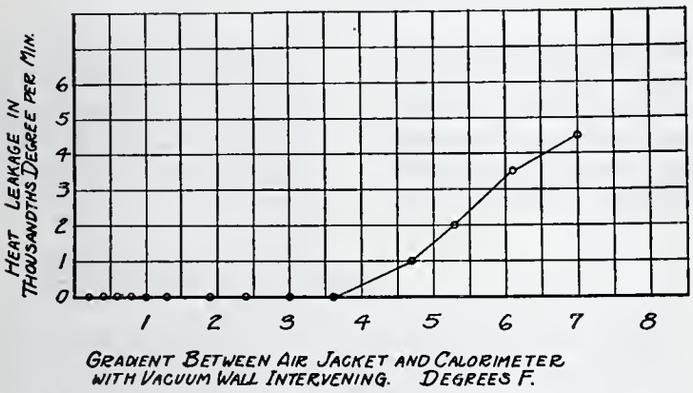


Figure 4—Effect of Low Gradient between Air Jacket and Calorimeter with Vacuum Wall Intervening

demonstrating the presence of a high heat head in the calorimeter, with a gradient of from 5° to 8° F. (2.77° to 4.44° C.), which accounted for the transmission of heat outwardly. These conditions are shown by the curve in Figure 1.

These results suggested the next series of experiments in which the temperature of the testing laboratory was maintained for half a day at 90° F. (32.22° C.). The next series of experiments was conducted under the same conditions as before by bringing the working temperature of the laboratory to 72° or 73° F. (22.22° or 22.78° C.), and using the same temperature in the calorimeter water. Here the heat leakage was equally pronounced but in the other direction, being inward. The results obtained are shown by the curve in Figure 2.

This seemed to furnish an explanation for the erratic behavior referred to by other operators, and the tests were continued by installing an air-circulating system whereby the air-jacketing spaces could be made to bring the jacketing material more nearly to an equilibrium with the surrounding atmosphere. The type of insulation is shown in Figure 3. The Illium bomb, *D*, is suspended in the vacuum jacket, *C*, which rests on a cork ring, *I*. The air space, *B*, separates the vacuum-wall container from the Bakelite jacket, *A*. The vacuum flask rests on a cork ring, *I*, and the top of the flask is sealed off from the air space, *B*, by means of a felt pad, *H*. A Bakelite ring, *F*, holds the vacuum flask erect. The Illium bomb, *D*, is suspended in a holder, *K*, which is raised and lowered by movement of telescoping tubes, *J*, on either side of the Illium bomb holder. Stirring of the water is accomplished by the stirrer, *E*, operated by the pulley, *G*.

A heating coil was located just outside the jacket with a small fan whereby, upon turning the switch, the circulating air could be heated, thus more quickly bringing the container and jacketing spaces up from a low temperature. Similarly, without the heat and by circulating the air of the room, an equalization of temperatures could be readily obtained. By establishing a condition of equilibrium and then slowly raising the jacket temperature (approximately 4° F., or 2.22° C., per hour), a gradient of over 3° F. (1.66° C.) was required to obtain an indication of heat leakage, as shown by the curve in Figure 4.

Another test, in which the conditions approximate those present for an actual B. t. u. determination, was made by circulating air from the room until equilibrium conditions were reached. The temperature of the water surrounding the bomb was the same as the jacket and constant. The temperature of the jacket was quickly raised (within 1 minute) 5.5° F. (3.05° C.) and maintained at that temperature, a gradient which would be more than that encountered in the usual determination. The calorimeter water remained constant for 31 minutes and then began to change at the rate of 0.001° F. (0.0005° C.) per minute during the next 30 minutes.

To test the comparative stability of temperatures that might be secured by use of a water jacket instead of an air jacket, an equipment was assembled of the type illustrated in Figure 5, in which the temperature of the jacket was controlled by means of quick accessibility to either hot or cold water. The Bakelite container, *A*, was the same as in Figure 3. The inner container, *B*, was circular and constructed of brass with a capacity of about 8 liters. An air jacket, *D*, surrounded the water container, *E*, in which the Illium bomb, *C*, was located. A stirring of the water in the jacket and circulation through the cover was maintained by the pump, *I*. The water in the cover portion of the jacket returned through to opening *H*. The two pulleys, *G*, operate the pump, *I*, and the stirrer, *F*.

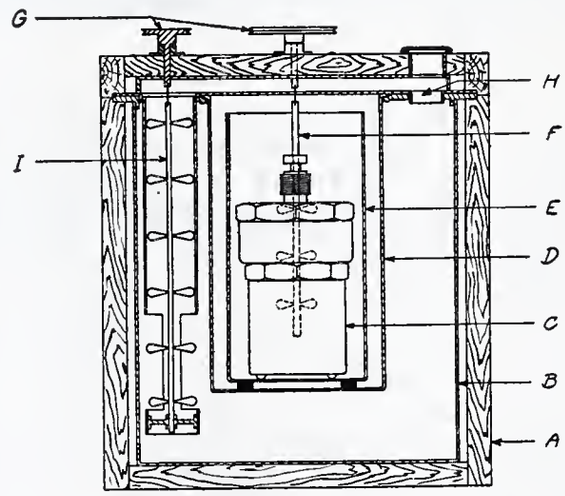


Figure 5—Apparatus for Testing Comparative Stability of Temperatures

Under these conditions, it is possible to obtain a quick and immediate response to any desired changes in temperature, and to easily maintain a gradient of less than 0.05° F. (0.027° C.). The method of maintaining adiabatic conditions, illustrated in Figure 5, has been in general use for a number of years. However, the instrument indicated in Figure 5 includes a number of simplifications in the means of stirring and circulation, the type of heater for supplying hot water, and the general construction, which permit a greater ease of operation without sacrificing any of the accuracy in the previous instrument of this type.

It should be noted that with either one of these devices the mechanical construction is such that the calorimeter container holding the water and bomb can be sealed off from the surrounding space between the calorimeter and the outer jacket, thus practically eliminating the error of heat of vaporization.

It is believed that with these devices a marked advance has been made in the accuracy and convenience of manipulation, and that this is due to the attaining of true adiabatic conditions.

Literature Cited

(1) Stansfield and Sutherland, *Can. J. Res.*, **3**, 464 (1930).
(2) White, "The Modern Calorimeter," p. 155, Monograph Series 42, Chemical Catalog.

Volumetric and Gravimetric Determination of Mercury as Periodate[1,2]

Hobart H. Willard and J. J. Thompson

Chemical Laboratory, University of Michigan, Ann Arbor, Mich.

Mercury may be quantitatively precipitated as mercuric periodate, $Hg_5(IO_6)_2$, from 0.15 *N* nitric or 0.1 *N* sulfuric acid solution. It may be weighed in this form, or determined volumetrically by iodometric methods. Moderate amounts of aluminum, cadmium, zinc, copper, nickel, calcium, and magnesium do not interfere.

Mercuric periodate was first prepared in 1834 by Bengieser (*2*) by the action of sodium periodate on mercuric nitrate. Later it was prepared by Lautsch (*6*) and by Rammelsberg (*7*) who treated mercuric oxide with a nitric acid solution of periodic acid. It was described as an orange-red salt having the composition $Hg_5(IO_6)_2$, not decomposed at 100° C., but completely volatile on ignition. It was insoluble in water.

In the course of an investigation on periodates in progress in this laboratory this salt was studied, particularly with reference to its suitability for the quantitative determination of mercury.

Experimental Data

Mercuric nitrate, dissolved in nitric acid of varying concentrations, was precipitated by the addition of excess of sodium periodate. Precipitation was complete at concentrations not greater than 0.15 *N*. At 100° C. the salt was appreciably soluble in water, but below 50° C. the solubility was practically negligible.

A sample of the salt was thoroughly washed with hot water, dried at 100° C. for 4 hours, and analyzed gravimetrically for iodine and mercury. It was dissolved in dilute nitric acid, tartaric acid was added, and the solution made ammoniacal. A slight excess of sulfite was added to reduce the periodate and the mercury was precipitated from the hot ammoniacal solution by hydrogen sulfide. After standing one hour, the mercuric sulfide was filtered through a filtering crucible with porous porcelain bottom, washed with hot water containing a little hydrogen sulfide, then with pure water, dried 2 hours at 100° C., and weighed. The filtrate was oxidized to sulfate by pure hydrogen peroxide, the excess removed by boiling, a little arsenite added to reduce any iodate, and after acidifying with nitric acid, the iodide was precipitated and weighed as silver iodide. The results were: found, 74.75, 74.73, 74.76 per cent of HgO, average 74.75 per cent, which is the theoretical value; 25.30, 25.26 per cent of I_2O_7, average 25.28 per cent, theory 25.25 per cent. The salt is thus shown to be the pentamercuric paraperiodate, $Hg_5(IO_6)_2$.

Some of this salt was recrystallized by dissolving it in concentrated nitric acid and diluting with water. The bright red crystals were washed and dried. They proved to be less pure than the precipitated salt. Analysis showed 73.83, 73.50, 73.76, 73.90 per cent of H_2O, average 73.75 per cent, compared with the theoretical 74.75 per cent; and 25.26, 25.38, 25.30, 25.28 per cent of I_2O_7, average 25.30 per cent, compared with 25.25 per cent.

The iodine in mercuric periodate was determined volumetrically in two ways:

Method A—The salt was dissolved in excess of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulfate:

$$Hg_5(IO_6)_2 + 34KI + 24HCl = 5K_2HgI_4 + 8I_2 + 24KCl + 12H_2O$$

Method B—The salt was dissolved in an excess of standard arsenite by adding considerable concentrated hydrochloric acid, and the excess was titrated back with iodate using a little chloroform as indicator (*1*, *5*):

$$Hg_5(IO_6)_2 + 6H_3AsO_3 + 12HCl = 5HgCl_2 + 2ICl + 6H_3AsO_4 + 6H_2O$$

In six titrations of the precipitated salt by these methods the maximum variation from the theoretical value was only 0.02 per cent.

Quantitative Determination of Mercury

Mercury is usually weighed as metal or as mercuric sulfide. Precipitation of the latter in hydrochloric acid solution is not entirely satisfactory (*3*), especially in the presence of zinc, cadmium, and copper, because of contamination with other sulfides. Volumetrically mercury may be determined in a number of ways, most of which are not particularly accurate, the thiocyanate titration (*4*) being a common and accurate one.

It has been found that mercury can be determined gravimetrically or volumetrically by precipitation as mercuric periodate, $Hg_5(IO_6)_2$, in the presence of aluminum, zinc, cadmium, nickel, copper, calcium, and magnesium. The method is rapid, convenient, and accurate, and the end point in the volumetric method is very sharp. Iron interferes because it is precipitated as ferric periodate. Attempts were made to keep it in solution as the complex fluoride, but under these conditions the mercury was not completely precipitated. Chloride and other halides must be absent, because they prevent complete precipitation of mercury, doubtless owing to the slight ionization of mercuric halides. The maximum permissible acidity for complete precipitation is 0.15 *N* nitric or 0.1 *N* sulfuric acid, and under these conditions a large excess of periodate is required.

Table I—Gravimetric Determination of Mercury as $Hg_5(IO_6)_2$

Mercury Taken	Mercury Found	Error	Acid Present
Gram	*Gram*	*Mg.*	
0.0497	0.0497	0	Nitric
0.1243	0.1240	− 0.3	Nitric
0.1563	0.1563	0	Nitric
0.2904	0.2903	− 0.1	Nitric
0.3882	0.3885	+ 0.3	Nitric
0.5493	0.5492	− 0.1	Nitric
0.5721	0.5721	0	Nitric
0.4799	0.4798	− 0.1	Sulfuric
0.6313	0.6311	− 0.2	Sulfuric
0.4852	0.2563	−228.9	Hydrochloric[a]

[a] Effect of hydrochloric acid in preventing precipitation is shown.

Procedure—A sample of pure mercury was dissolved in nitric acid, sp. gr. 1.2, and the solution evaporated to dryness. It was taken up with 150 cc. of 0.15 *N* nitric acid or

[1] Received August 12, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of doctor of philosophy.

0.1 N sulfuric acid, heated to boiling, and the mercury precipitated by adding slowly, with constant stirring, 2 grams of sodium or potassium periodate dissolved in 50 cc. of water. It was cooled, filtered through a filtering crucible with a sintered-glass or porous porcelain bottom, washed with warm water, dried at 100° C. for 2 or 3 hours, and weighed as $Hg_5(IO_6)_2$. The results are shown in Table I.

Volumetric Determination

Method A—The filtered and washed precipitate of mercuric periodate in the crucible was treated with 2 or 3 grams of solid potassium iodide and 10 to 15 cc. of water, stirring until all the periodate had dissolved. The solution was washed into a 150-cc. conical flask (most conveniently a suction flask), acidified with 10 cc. of 2 N hydrochloric acid, and the liberated iodine titrated with 0.1 N sodium thiosulfate, using starch as indicator.

Method B—The precipitate in the crucible was treated with an excess of standard arsenite and then concentrated hydrochloric acid added until it dissolved, about 35 cc. being required if the volume at the end of the titration is about 100 cc. The solution was washed into a 150-cc. glass-stoppered conical flask, and titrated with 0.1 N potassium iodate until it had a light brown color. Four or five cubic centimeters of chloroform were then added and the titration continued, shaking after each addition until the purple color of the iodine just disappeared (*1*, *5*). The solution at the end point should contain between 28 and 45 cc. of hydrochloric acid, sp. gr. 1.18, per 100 cc.

The results, both with pure mercury and in mixtures with other metals, are shown in Table II. In the first three experiments method B was used; in all others, method A. The mercuric salt was precipitated from a nitric acid solution.

Table II—Volumetric Determination of Mercury as $Hg_5(IO_6)_2$

Mercury Taken	Mercury Found	Other Metals Present	Error
Gram	*Gram*	*Gram*	*Mg.*
0.3645	0.3646		+0.1
0.2071	0.2070		−0.1
0.0513	0.0513	0.20 Ni	0
0.2556	0.2558	0.15 Al	+0.2
0.1327	0.1327	0.18 Cd	0
0.1903	0.1902	0.17 Zn	−0.1
0.1064	0.1065	0.13 Cu	+0.1

If a chloride solution is to be analyzed, the mercury may first be precipitated as metal or sulfide and then converted into nitrate or sulfate.

Literature Cited

(1) Andrews, *J. Am. Chem. Soc.*, **25**, 756 (1903).
(2) Bengieser, *Ann.*, **17**, 259 (1834).
(3) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 170, Wiley, 1929.
(4) Hillebrand and Lundell, *Ibid.*, p. 173.
(5) Jamieson, "Volumetric Iodate Methods," p. 18, Chemical Catalog, 1926.
(6) Lautsch, *J. prakt. Chem.*, **100**, 86 (1867).
(7) Rammelsberg, *Ann. Physik*, **134**, 524 (1868).

Volumetric Determination of Manganese after Oxidation by Periodate[1,2]

Hobart H. Willard and J. J. Thompson

Chemical Laboratory, University of Michigan, Ann Arbor, Mich.

Manganese up to 30 mg. can be determined by oxidation to permanganate with periodate in either phosphoric or sulfuric acid solution, removal of excess periodate by precipitation as mercuric salt, and reduction of the permanganate by standard ferrous sulfate. The reaction goes best in a phosphoric acid solution, in which case less than a milligram of chromium does not interfere. Cobalt, cerium, and chloride must be absent.

Willard and Greathouse (*4*) have shown that manganese can be determined colorimetrically by oxidation to permanganate with a small excess of periodate. The solution thus obtained is stable for weeks, a fact confirmed by others (*3*). It seemed desirable, therefore, to make this the basis of a volumetric method by removing the excess of periodate. This was accomplished by precipitation as mercuric periodate, after which the permanganate was titrated by adding excess of standard ferrous sulfate and back titrating with permanganate. Although bismuth periodate is the least soluble of all, its presence caused certain errors which made its use for this purpose impossible.

Precipitation of Periodate as Bismuth Salt

A known volume of standard permanganate was reduced with ferrous sulfate in a dilute sulfuric acid solution, and the manganous salt was then oxidized to permanganate by adding 0.3 gram of sodium metaperiodate, $NaIO_4$, and boiling gently for 15 minutes. After cooling to room temperature, the excess periodate was precipitated by the addition of bismuth perchlorate, as a white, voluminous precipitate of bismuth periodate. The solution was immediately titrated with standard ferrous sulfate. To make the end point more distinct in the presence of the precipitate, alphazurine (Erioglaucine A) (*2*) was added just before the end point. Too little ferrous sulfate was always used, showing that some permanganate had been reduced, because other experiments proved that oxidation was complete. The surprising fact was that in the presence of iodate some of the permanganate was used in the oxidation of bismuth. In the presence of bismuth periodate only, no such error occurred. Both bismuth and iodate are necessarily present because the latter is formed by reduction of the periodate by manganous ion (*4*). It could not be completely removed by precipitation as silver iodate. If standard permanganate to which as much as 0.6 gram of sodium periodate had been added was treated with a bismuth salt, and, without filtering, titrated with ferrous sulfate, accurate results were obtained. If, however, excess of the latter was added and back titrated with permanganate, the results indicated that the excess of ferrous salt was slowly oxidized by the precipitate of bismuth periodate even in cold solution.

There are, therefore, two errors to be considered: oxidation of the excess reducing agent by iodate or insoluble

[1] Received August 12, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of doctor of philosophy.

bismuth periodate, and oxidation of bismuth. Of the possible volumetric reducing agents, vanadyl sulfate and ferrous sulfate were slowly oxidized by bismuth periodate, but oxalate and hydrogen peroxide were not affected. On the other hand, the former were not oxidized by the low concentration of iodate, but the two latter were oxidized. The use of bismuth as a precipitant, therefore, had to be abandoned.

Precipitation of Periodate as Mercuric Salt

It was found that periodate could be completely precipitated as the mercuric salt, $Hg_5(IO_6)_2$ (*5*). Although more soluble than the bismuth salt, it is still sufficiently insoluble even in the concentration of acid used for the oxidation of manganese, provided a large excess of mercuric ion is present. The mercuric salt has a very decided advantage in that it is much more easily filtered. There is also no possibility of further oxidation of the mercury by permanganate. Experiments showed that amounts of manganese up to 30 mg. could be accurately determined by oxidation to permanganate in a solution containing either phosphoric, sulfuric, or phosphoric and sulfuric acids. There was no blank correction to be applied. In this respect there is a slight advantage over the bismuthate method (*1*). Iron ores can be quickly dissolved in phosphoric acid[3] and this method applied directly to the solution, but this is not possible with bismuthate.

Table I—Effect of Chromium on Determination of Manganese

Material Used	Acid Present	Approx. Wt. of Sample	Chromium Present	Manganese Present	Manganese Found
		Grams	*Mg.*	%	%
B. S. Steel, No. 10c	Phosphoric	1.1	4.0	1.13	1.160
B. S. Steel, No. 10c	Phosphoric	1.0	3.0	1.13	1.153
B. S. Steel, No. 10c	Phosphoric	1.0	2.0	1.13	1.148
B. S. Steel, No. 10c	Sulfuric	1.3	2.0	1.13	1.232
B. S. Steel, No. 10c	Phosphoric	1.0	1.5	1.13	1.143
B. S. Steel, No. 10c	Phosphoric	1.0	1.0	1.13	1.138
B. S. Steel, No. 10c	Phosphoric	1.0	0.5	1.13	1.139
B. S. CrNi Steel, No. 32b	Phosphoric	1.14	7.3	0.624	0.661
B. S. CrNi Steel, No. 32b	Phosphoric	1.04	6.6	0.624	0.664
B. S. CrNi Steel, No. 32b	Phosphoric	1.18	7.6	0.624	0.749
B. S. CrNi Steel, No. 32b	Phosphoric	1.20	7.7	0.624	0.686

Experiments using standard permanganate were carried out to determine the accuracy of the method. Samples of 25 to 40 cc. of 0.05 *N* permanganate were reduced with ferrous sulfate in a solution containing, in a volume of 100 cc., about 10 to 15 cc. of 85 per cent phosphoric acid, or mixtures of 3 or 4 cc. of phosphoric acid with 5 or 4 cc. of concentrated sulfuric acid, and oxidized by adding 0.3 to 0.5 gram of sodium or potassium periodate and heating just to boiling for 15 minutes. The solution was cooled to room temperature, diluted to 150 cc., and 2 to 5 grams of mercuric nitrate, $Hg(NO_3)_2.2H_2O$, dissolved in a little water, were added to precipitate the excess periodate and nearly all of the iodate. The solution was filtered into an excess of 0.05 *N* ferrous sulfate through an asbestos mat 3 to 4 mm. thick on a 9-cm. No. 17G sintered-glass filtering funnel. A Büchner funnel would doubtless be almost as satisfactory. The precipitate of mercuric periodate was washed four times with water, and the excess of ferrous sulfate was titrated back with standard permanganate. The results obtained were the same within 0.01 cc. as in the direct titration of the ferrous sulfate with permanganate. When chromium was present, it was found that in the presence of sulfuric acid about 60 per cent of it was oxidized when the content was about 1.5 mg., thereby giving high results for manganese. However, this tendency is very much minimized in phosphoric acid solutions, so that an accurate determination of manganese can be made in the presence of 1 mg. of chromium. Because of the difficulty in washing out all the permanganic acid from very large precipitates of mercuric periodate, only 0.3 gram of sodium or potassium periodate should be used for 15 mg. or less of manganese. Accurate results can be obtained, however, with as much as 30 mg. of manganese, using, in this case, 0.5 gram of periodate. With larger amounts such voluminous precipitates are formed that all the permanganic acid cannot be removed by washing. Instead of the metaperiodate, the paraperiodate, $Na_3H_2IO_6$, may be used. Manganese is more readily oxidized and the permanganic acid formed is more stable in a phosphoric acid solution, so that this acid is desirable when considerable amounts of manganese are present.

The concentration of acid may vary within wide limits as far as oxidation of manganese is concerned, although with large amounts of the latter, manganese dioxide may form unless phosphoric acid is present. A fairly high concentration of acid increases the rate of oxidation. The solubility of mercuric periodate, however, is increased under these conditions, so that it is advisable to dilute the solution before removing the excess of periodate. Concentrations not greater than 5 cc. of sulfuric acid, sp. gr. 1.83, or 15 cc. of 85 per cent phosphoric acid per 100 cc. are recommended. Mixtures of the two acids are desirable, because the mercuric periodate is more crystalline in the presence of sulfuric acid, and without some phosphoric acid, manganese dioxide may form.

The weight of mercuric nitrate required for complete precipitation of periodate varies from 5 grams with 5 cc. of sulfuric acid to 2 grams with 15 cc. of phosphoric acid per 100 cc.

Titration of the permanganic acid with arsenite instead of ferrous sulfate is impossible because of an indefinite end point.

Chloride must be absent. Cobalt interferes as in the bismuthate method (*1*). When periodate is added to a solution of cobaltous sulfate, the solution becomes dark brown, owing to oxidation of the cobaltous salt. In steel containing 1.13 per cent of manganese and 0.5 per cent of cobalt, 1.32 per cent of manganese was obtained. Cerium also interferes because it is oxidized to a ceric salt.

Procedure for Steel or Iron Free from Chromium

Dissolve 1 gram of steel containing not more than 0.15 mg. of chromium in 4 cc. of concentrated sulfuric acid and 25 cc. of water. To the hot solution, add, cautiously, 1 cc. or more of concentrated nitric acid to oxidize the ferrous iron and carbonaceous matter, and boil to remove nitrous fumes. Any graphite present will do no harm and will be filtered out later. Dilute to 50 or 75 cc., add 3 cc. of 85 per cent phosphoric acid (or an equivalent amount of more dilute acid) and 0.3 gram of sodium or potassium periodate. Boil gently for 15 minutes to oxidize the manganese, dilute to 150 cc., cool to room temperature, and add slowly, with constant stirring, 4 or 5 grams of mercuric nitrate ($Hg(NO_3)_2.2H_2O$) dissolved in a little water. Filter immediately through a fairly large asbestos filter into an excess of standard ferrous sulfate, wash with cold water four or five times, and titrate back with standard permanganate.

Procedure for Steel or Iron Containing Not Over 0.1 Per Cent of Chromium

Dissolve 1 gram in a mixture of 15 cc. of water and 15 cc. of 85 per cent phosphoric acid. Oxidize the ferrous iron and carbonaceous matter by adding carefully to the hot solution 1 or 2 cc. of concentrated nitric acid, and boil to remove nitrous fumes. Dilute to 100 cc., add 0.3 gram of sodium or potassium periodate, boil gently 15 minutes to oxidize the manganese, dilute to 150 cc., and cool to room temperature. Precipitate the periodate by adding slowly,

[3] Unpublished work by one of the authors.

with constant stirring, 2 to 3 grams of mercuric nitrate dissolved in a little water, and filter immediately through a fairly large asbestos filter into excess of standard ferrous sulfate containing 10 cc. of 50 per cent sulfuric acid to prevent precipitation of mercuric phosphate. Wash with cold water four or five times and titrate back the filtrate and washings with standard permanganate. The filtration will be slower than when sulfuric acid is present during precipitation, but the time required, including washing, should not be more than 3 minutes. The effect of chromium with and without phosphoric acid is shown in Table I.

Procedure for Iron Ore and Other Oxide Ores

Place 1 gram in a 250-cc. Pyrex beaker, and add 15 cc. of 85 per cent phosphoric acid and a few drops of concentrated sulfuric acid. Stir until all the ore is free from the bottom of the beaker, cover, and heat until fumes of sulfuric acid are given off, taking care that it does not froth over or cake on the bottom. If the ore is not dissolved by this time, keep it hot for a longer time, stirring occasionally, but not allowing the temperature to rise, because the beaker would be attacked. Cool until the mass begins to be viscous, then add quickly 100 cc. of water, and heat. Everything should dissolve except some gelatinous silica. From here on the procedure is the same as for steel containing 0.1 per cent of chromium.

Procedure for Bronze

Dissolve 1 gram in a mixture of 3 cc. of concentrated nitric acid, 10 cc. of 85 per cent phosphoric acid, and about 7 or 8 cc. of water. Then dilute to 50 or 75 cc. and proceed as above. Owing to the deep blue color of the copper salt, the back titration with permanganate is conveniently carried out electrometrically or by use of alphazurine indicator (*2*).

Note—If the amount of manganese is between 15 and 30 mg., the amount of periodate in the above procedures should be increased to 0.5 gram.

Results obtained by this method with different materials are shown in Table II. In all cases phosphoric acid was used with the sulfuric to prevent formation of manganese dioxide.

Table II—Determination of Manganese in Various Materials

Material Analyzed	Acid Used	Approx. Wt. of Sample	Chromium Present	Manganese Present	Manganese Found
		Grams	%	%	%
B. S. Steel, No. 10c	Phosphoric	1.06	0.01	1.13	1.136
B. S. Steel, No. 10c	Phosphoric	1.03	0.01	1.13	1.132
B. S. Steel, No. 10c	Sulfuric	1.29	0.01	1.13	1.138
B. S. Steel, No. 10c	Sulfuric	1.01	0.01	1.13	1.139
B. S. Cast Iron, No. 4c	Phosphoric	1.04	0.016	0.897	0.890
B. S. Cast Iron, No. 4c	Phosphoric	1.18	0.016	0.897	0.894
B. S. Cast Iron, No. 4c	Sulfuric	1.14	0.016	0.897	0.898
B. S. Cast Iron, No. 4c	Sulfuric	1.13	0.016	0.897	0.912
B. S. Steel, No. 21b	Phosphoric	1.26	0.021	0.564	0.570
B. S. Steel, No. 21b	Phosphoric	1.12	0.021	0.564	0.562
B. S. Steel, No. 16b	Phosphoric	1.10	0.007	0.381	0.389
B. S. Steel, No. 16b	Phosphoric	1.24	0.007	0.381	0.388
B. S. Steel, No. 16b	Sulfuric	1.02	0.007	0.381	0.390
B. S. Steel, No. 16b	Sulfuric	1.22	0.007	0.381	0.392
Steel A	Phosphoric	1.47[a]	0.065	1.99	1.99
Steel A	Phosphoric	1.46[a]	0.065	1.99	1.98
Steel A	Sulfuric	0.49	0.065	1.99	2.02
Steel A	Sulfuric	0.43	0.065	1.99	2.00
B. S. Mn Bronze, No. 62	Phosphoric	0.69	...	1.59	1.61
B. S. Mn Bronze, No. 62	Phosphoric	0.62	...	1.59	1.64
B. S. Norric Iron Ore, No. 28	Phosphoric	1.00	...	0.465	0.446
B. S. Norric Iron Ore, No. 28	Phosphoric	1.09	...	0.465	0.447
B. S. Bauxite, No. 69	Phosphoric	1.27	...	0.426	0.421
B. S. Bauxite, No. 69	Phosphoric	1.26	...	0.426	0.420

[a] These samples contain nearly 30 mg. of manganese.

Literature Cited

(1) Hillebrand and Lundell, "Applied Inorganic Analysis," p. 345, Wiley, 1929.
(2) Knop, *Z. anal. Chem.*, **77**, 125 (1929).
(3) Richards, *Analyst*, **55**, 554 (1930).
(4) Willard and Greathouse, *J. Am. Chem. Soc.*, **39**, 2366 (1917).
(5) Willard and Thompson, Ind. Eng. Chem., Anal. Ed., **3**, 398 (1931).

Use of Selenium as Catalyst in Determination of Nitrogen by Kjeldahl Method[1]

Michael F. Lauro[2]

2 Broadway, New York, N. Y.

TIME is always a factor in commercial analysis. Experiments are forever being carried on to find short cuts without sacrificing accuracy. In cereal work this is especially true. While on work of an entirely different nature, the analysis of rare earths, the author hit upon a solution of the problem of shortening the time in Kjeldahl digestions.

The general method for the determination of nitrogen (organic and ammoniacal) by the Kjeldahl process of oxidation with concentrated sulfuric acid is outlined in the methods of analysis of the Association of Official Agricultural Chemists (*3*). From 0.7 to 3.5 grams of the substance to be analyzed are placed in the special digestion flask with 0.7 gram of mercuric oxide or its equivalent in metallic mercury, and 20 to 30 cc. of concentrated sulfuric acid. From 0.1 to 0.3 gram of crystallized copper sulfate may be substituted for or added to the mercury. The digestion is carried on until the mixture is colorless or nearly so, when oxidation is presumed complete. This usually requires 2 hours.

The Gunning modification of this method makes use of 10 grams of powdered sulfate or anhydrous sodium sulfate and suggests the use of 0.1 to 0.3 gram of copper sulfate in place of the mercury.

[1] Received April 21, 1931.

[2] Consulting chemist.

A further modification, Kjeldahl-Gunning-Arnold, specifies 15 to 18 grams of sodium or potassium sulfate, 1 gram of copper sulfate or 0.7 gram of mercuric oxide in 25 cc. of sulfuric acid.

The American Association of Cereal Chemists (*1*) specifies a 1-gram sample, 10 grams of a mixture of potassium and sodium sulfates, 20 cc. of sulfuric acid, and 0.5 gram of mercuric oxide. The American Oil Chemists Society (*2*) recommends 1.7304 grams (the ammonia equivalent) of substance to be analyzed, 10 grams of potassium or sodium sulfate, 25 cc. of concentrated acid, and 0.5 gram of mercury or 0.7 gram of mercuric oxide.

As can be seen, the catalyst used to hasten the process of breaking down of the nitrogenous material and its conversion into ammonium sulfate may be either copper as sulfate or mercury as oxide or as the metal. Where mercury is used, this must be precipitated out with sodium or potassium sulfide before subsequent distillation with lye. With copper, however, this step is unnecessary.

The time of digestion is, of course, affected by the amounts used, but as the method is now standardized, about the only remaining factor arises from the kind of flame used in heating. A hotter flame naturally shortens the time materially. Nevertheless, allowing for this with the type of burners at

Table I—Results of Analysis by Modified Method

Material	Method	Protein %	Ammonia %	Time Minutes
Flour 1	Hg	15.35		90
	Cu	15.19		70
	Se (oxychloride)	15.50		20
Flour 2	Hg	14.25		75
	Cu	14.25		60
	Se (oxychloride)	14.39		18
Flour 3	Hg	8.34		70
	Cu	8.28		55
	Se	8.35		12
Wheat 1	Hg	14.05		135
	Cu	14.01		120
	Se (oxychloride)	14.18		23
Wheat 2	Hg	13.06		130
	Cu	12.96		105
	Se	13.12		20
Wheat 3	Hg	11.93		90
	Cu	11.82		65
	Se	11.88		22
Cottonseed meal 1	Hg	42.19	8.21	125
	Cu	41.44	8.06	100
	Se	42.06	8.18	35
Cottonseed meal 2	Hg	46.63	9.07	130
	Cu	45.75	8.90	110
	Se	46.44	9.03	40
Cracklings 1 (bones)	Hg	44.19	8.60	180
	Cu	43.69	8.50	150
	Se (oxychloride)	44.50	8.66	40
Cracklings 2	Hg	45.44	8.84	165
	Cu	44.81	8.72	140
	Se	45.25	8.80	55
Cracklings 3	Hg	34.44	6.70	140
	Cu	34.00	6.62	120
	Se	34.25	6.66	45

this laboratory the minimum time obtainable for flour digestion is about 1 hour, for wheat from 1 to $1^1/_2$ hours, and for cracklings about 2 hours. Quite often, complete solution as evidenced by color and appearance may take from 2 to 4 hours.

As the author happened to be working with selenium oxychloride extractions of tantalum and columbian ores, he made use of that particular compound. Subsequently selenium, recovered from the waste or spent acids from the above process, was used. The results were about the same, slightly below those obtained by the oxychloride.

In Table I is a list of products analyzed by the modification of the conventional method, all run at the same time and under the same heating conditions and with the same amounts of reagents (other than the catalysts) as the process with copper sulfate and mercuric oxide—i. e., 10 grams of either sodium or potassium sulfate and 25 cc. of acid, and 0.1 to 0.2 gram of selenium. No sodium or potassium sulfide need be added before distillation.

Literature Cited

(1) Am. Assocn. Cereal Chem., Methods for Analysis of Cereals and Cereal Products, 1928.
(2) Am. Oil Chem. Soc., Official Methods of Chemical Analysis, 1929.
(3) Assocn. Official Agr. Chem., Methods, 2nd ed., 1925.

Continuous Measurement of pH with Quinhydrone Electrodes[1]

C. C. Coons

Leeds & Northrup Company, 4901 Stenton Ave., Philadelphia, Pa.

The concentration of quinhydrone necessary for a pH measurement of an accuracy of ±0.05 pH on most dilute water solutions is shown to be 7 mg. per 100 cc. of solution.

A quantitative method for determining the concentration of quinhydrone dissolved in water is outlined and the solubility curve for quinhydrone is given from 0° to 50° C.

The practicability of various methods of adding quinhydrone to a flowing solution for the purpose of obtaining continuous pH measurements is discussed. A solution of quinhydrone added continuously from an external source to the flowing test solution is considered the best method of introducing quinhydrone into the test solution.

A noble metal electrode of platinum is shown to retain its power of reproducibility much better than a gold electrode during continuous pH measurements.

A platinum electrode for continuous pH measurements is best cleaned by boiling it in a 5 to 10 per cent sodium bisulfite solution. If an acid wash is first necessary, it is followed by the sulfite treatment.

THE quinhydrone electrode is an accurate and widely used method for measuring the pH of many types of solutions within the range of 0 to 8.5 pH, and sometimes 9 pH. The electrode may be applied either to individual pH measurements or to continuous measurements, the latter being employed for automatic recording and control. In order to obtain reliable continuous measurements with the quinhydrone electrode, it is important to make sure that a proper amount of quinhydrone is supplied to the test solution and that the noble metal electrode at all times accurately indicates the quinhydrone potential. It is the purpose of this paper to discuss in some detail these features of the continuous pH electrode—namely, (1) the amount of quinhydrone necessary for a reliable pH measurement; (2) the solubility of quinhydrone under various conditions; and (3) the noble metal electrode.

[1] Received April 24, 1931.

Quinhydrone Electrode

The quinhydrone electrode comprises a noble metal electrode immersed in a solution containing dissolved quinhydrone. The potential established on the metal electrode is compared with that of a reference electrode which is usually a saturated calomel cell. The voltage between these two cells is measured with a potentiometer in the usual way.

To obtain continuous pH measurements of a flowing solution, it is most convenient to pass a portion of the solution through a flow channel in which the noble metal electrode and the reference electrode are suspended. The proper amount of quinhydrone must be dissolved in the solution prior to passing it through the flow channel.

Introduction of Quinhydrone in Test Solution—There are, in general, two types of methods by which quinhydrone may be introduced into the test solution prior to its passage through the flow channel. In one type the quinhy-

drone is retained at all times in the flowing test solution, and in the other quinhydrone is added to the test solution from an external supply. In the former type the crystals of quinhydrone may be held in cloth sacks or pressed into hard pellets, or the test solution may filter through the crystals which are prevented by a filter screen from passing into the flow channel. In the second type the quinhydrone may be added to the flowing test solution by a screw mechanism similar to a lime feeder for water treatment, or the quinhydrone may be dissolved in a suitable solvent, and this solution subsequently added to the test solution.

In comparing these two types it is apparent that there are certain inherent disadvantages involved in retaining crystals or pellets of quinhydrone in the flowing test solution. First, these crystals or pellets have a filtering action and, if solid particles are present in the solution, the flow is retarded or even stopped. Second, it is impossible to eliminate the formation of deposits over the surfaces of quinhydrone exposed to the test solution, and these films seriously retard the rate at which quinhydrone is dissolved. Third, it is impossible to control the rate of solution of the quinhydrone which varies considerably with the temperature and the rate of flow of the test solution. In addition to these troubles the quinhydrone or cloth sacks absorb the solution and may cause a serious lag in the ability of the electrode to follow a changing pH. However, pellets are more satisfactory than loose crystals or cloth sacks of crystals because they have less tendency to pack together.

During the progress of this work the practicability of pellets used under ideal conditions was tested. These tests involved the determination of the solubility curve for quinhydrone and the variation in the rate of solubility of the pellets with a variation in rate of flow and temperature of the test solution.

The addition of quinhydrone to the test solution from an external supply avoids all of the above difficulties. A solution feeding device is considered superior to a dry feeding device for the following reasons: Not only does the quinhydrone disperse rapidly in the test solution since it is already in solution, but the apparatus for introducing a solution of quinhydrone is much simpler than that used for continuously adding crystals of quinhydrone.

Amount of Quinhydrone Necessary for pH Measurement—For making continuous pH measurements it is essential to know the minimum concentration of quinhydrone that will yield a sufficiently accurate pH measurement, not only from the standpoint of reliability but also for an economical operation of the unit.

In order to obtain a pH measurement of the highest accuracy, it is customary to saturate the solution with quinhydrone. However, Biilman and Jensen (*1*) have shown that, if an accuracy of only 1 millivolt is required, one-tenth the amount of quinhydrone required for saturation may be used at 18° C. It should follow that, if less accuracy is desired, less quinhydrone may be used. However, these statements are true only in special cases, and to obtain a desired accuracy the type of solution must be considered in limiting the concentration of quinhydrone. In order to avoid a lengthy discussion on this subject, it will suffice to say that the following procedure for quinhydrone pH measurements may be applied with sufficient accuracy (±0.05 pH) to most industrial solutions in which the quinhydrone electrode may be expected to yield reliable results.

In order to determine the minimum concentration of quinhydrone necessary for a sufficiently accurate pH measurement, eight buffer solutions ranging from 1 to 8 pH were prepared according to Clarke (*2*). The pH value of each buffer solution was accurately determined with a dip-type quinhydrone electrode and a saturated calomel electrode, the solution being saturated with quinhydrone for each measurement. The pH value of each buffer solution was then obtained in the same manner, except that definite small quantities of quinhydrone were added to 50 cc. of each buffer solution until the pH value was essentially that obtained by saturating the solution with quinhydrone. The data resulting from these experiments are given in Table I.

Table I—Results of Experiments to Obtain pH Values of Buffer Solutions

	Composition of Buffer Solns.	Buffer Saturated with Quinhydrone Voltage at 21° C. with saturated calomel cell	pH	Drops of Acetone Soln. Added to 50 cc. of Buffer	Voltage at 21° C. with Saturated Calomel Cell
I	4.2 grams citric acid, 1.6 grams sodium hydroxide, 15.4 cc. 36% hydrochloric acid, 2.0 liters distilled water	−0.3797	1.25	4	−0.3795
				10	−0.3802
II	42.0 grams citric acid, 16.0 grams sodium hydroxide, 2.0 liters distilled water	−0.3415	1.94	4	−0.3415
				4	−0.3425
III	20.0 grams potassium acid phthalate, 3.5 cc. 36% hydrochloric acid, 2.0 liters distilled water	−0.2798	3.12	4	−0.2810
				10	−0.2808
IV	20.0 grams potassium acid phthalate, 4.0 cc. 0.2 *N* sodium hydroxide, 2.0 liters distilled water	−0.2204	4.00	4	−0.2210
				10	−0.2210
				20	−0.2210
V	50.0 cc. *N* sodium hydroxide, 100.0 cc. *N* acetic acid, 350.0 cc. distilled water	−0.1845	4.62	4	−0.1855
				10	−0.1850
				20	−0.1849
VI	20.0 grams potassium dihydrogen phosphate, 56.4 cc. 0.2 *N* sodium hydroxide, 1950.0 cc. distilled water	−0.1195	5.72	4	−0.1200
				10	−0.1193
				20	−0.1190
VII	4.59 grams disodium phosphate, 7.06 grams potassium dihydrogen phosphate, 2.0 liters distilled water	−0.0882	6.28	4	−0.0880
				10	−0.0875
				20	−0.0871
VIII	6.2 grams boric acid, 7.45 grams potassium chloride, 40.0 cc. 0.2 *N* sodium hydroxide, 1960.0 cc. distilled water	+0.0085	7.85	4	+0.0060
				10	+0.0080
				15	+0.0081

The same procedure was repeated on the buffer solutions after they were diluted tenfold, and also on buffer solutions ten times as concentrated. These data are given in Tables II and III, respectively.

It would be a difficult and tedious task to weigh out milligrams of quinhydrone and add them successively to the 50-cc. samples of buffer solutions. Therefore, instead of doing this, a concentrated solution of quinhydrone dissolved in acetone was prepared. This solution was kept in a glass-stoppered bottle, the glass stopper comprising a dropper. Twenty drops of this acetone solution had a volume of 0.5 cc., and each drop contained 0.0009 gram of quinhydrone.

The results given in Tables I, II, and III show that, regardless of the pH of the buffer solution (not above 8.0 pH), four drops of the quinhydrone solution in 50 cc. of the buffer

solution gave a pH measurement easily within an accuracy of ±0.05 pH. The weight of quinhydrone in these four drops of acetone solution was 0.0036 gram. If less than four drops were used, the potential occasionally was unstable and a longer time was required for an equilibrium potential to be established. The concentration of acetone used had practically no effect on the pH measurement.

Table II—Results of Experiments with Same Buffer Solutions Diluted
(50 cc. of buffer + 350 cc. of distilled water)

Buffer Soln.	Buffer Saturated with Quinhydrone: Voltage	Buffer Saturated with Quinhydrone: pH at 21° C.	Drops of Acetone Soln.	Voltage at 21° C.
I	−0.3305	2.12	5	−0.3300
			10	−0.3300
			1 cc.	−0.3310
II	−0.3014	2.61	4	−0.3010
			10	−0.3010
			1 cc.	−0.3018
III	−0.2690	3.17	4	−0.2694
			10	−0.2690
			1 cc.	−0.2680
IV	−0.2140	4.12	4	−0.2140
			10	−0.2130
			20	−0.2125
			1 cc.	−0.2100
V	−0.1820	4.66	4	−0.1822
			10	−0.1819
VI	−0.1101	5.88	4	−0.1104
			20	−0.1095
			30	−0.1090
VII	−0.0820	6.36	5	−0.0818
			20	−0.0805
			1 cc.	−0.0784
VIII	+0.0085	7.88	4	+0.0092
			10	+0.0100
			15	+0.0100
			1 cc.	+0.0115

Table III—Results of Experiments with Concentration of Buffer Solutions Increased Tenfold

Composition of Buffer Solns.	Buffer Saturated with Quinhydrone: Voltage	Buffer Saturated with Quinhydrone: pH at 21° C.	Drops of Acetone Solution Added to 50 cc. of Buffer	Voltage
12 cc. glacial acetic acid, 27.0 grams sodium acetate, 400 cc. distilled water	−0.1896	4.52	2	−0.1910
			4	−0.1890
			10	−0.1890
			20	−0.1890
9.2 grams disodium phosphate, 14.0 grams potassium dihydrogen phosphate, 400 cc. distilled water	−0.1086	5.92	4	−0.1094
			10	−0.1086
			20	−0.1086

Although these data were obtained at 21° C., essentially the same results were found at other temperatures and on different types of solutions, whether buffered or unbuffered. Hence, it may be concluded that for an accuracy of ±0.05 pH, 7 mg. of quinhydrone per 100 cc. of test solutions are sufficient in the temperature range of 2° to 40° C. for a large number of industrial solutions. In a few special cases it has been necessary to increase this concentration of quinhydrone, the requisite concentration being determined as above by a dip-type pH apparatus.

Quantitative Determination of Quinhydrone Dissolved in Water—The method developed for the quantitative determination of quinhydrone utilized the oxidizing power of potassium permanganate. The following solutions were prepared: A potassium permanganate solution containing 15 grams per liter of solution, and a reducing solution containing per liter of solution 100 grams of ferrous ammonium sulfate, 20 grams of ammonium sulfate, and 25 cc. of 95 per cent sulfuric acid. The equivalent of reducing solution to the permanganate solution was obtained. The permanganate solution was standardized by the procedure given below against aliquot parts of (10 cc.) standard solutions of quinone, hydroquinone, and quinhydrone, each standardization yielding the same result within the experimental error. These standard solutions of quinone, etc., contained 2 to 4 grams of pure compound in a liter of distilled water

The procedure for determining the concentration of quinhydrone solutions is as follows: The sample was diluted if necessary to 250 cc. with water, 25 cc. of 95 per cent sulfuric acid added, and the solution heated to 80° to 85° C. Standard permanganate solution was added rapidly, with constant stirring, 2 or 3 cc. past the end point (the first pink color). The solution was boiled for a minute to insure the complete oxidation of the quinhydrone, after which the excess permanganate was titrated with the reducing solution until the solution became clear. Then the standard permanganate solution was added slowly until the first pink tinge of color appeared.

The volume of quinhydrone solution used for a determination depended upon the quinhydrone concentration. If too concentrated a sample was employed, an unnecessarily large amount of permanganate was required. In some cases the quinhydrone solution was so dilute that the sample employed had a volume of 250 cc., and at other times a volume of only 10 cc. was used, which was diluted to 250 cc.

Solubility of Quinhydrone in Distilled Water—In order to calculate the per cent concentration of quinhydrone in the test solution after it had passed through the tube containing pellets of quinhydrone, it was necessary to determine the solubility curve for quinhydrone. This was accomplished by saturating distilled water at various temperatures and determining the amount of quinhydrone dissolved in a definite volume of solution. The saturated solutions were prepared in a thermostat with frequent stirring. Two hours were allowed at each temperature (with the exception of 50° C.) for saturation, after which period of time check results were obtained. At 50° C. the oxidation of quinhydrone became appreciable, causing results that were too high. Definite volumes of these saturated solutions were removed with a pipet, the tip of which was covered with a glass tube filled with cotton to filter out solid particles of quinhydrone.

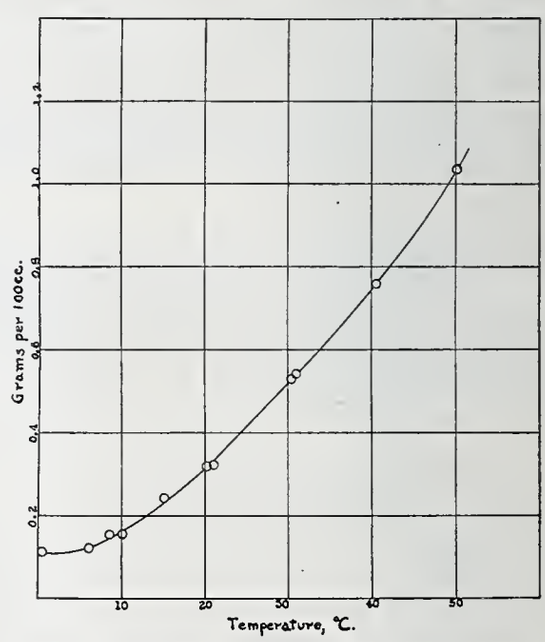


Figure 1—Solubility Curve for Quinhydrone Dissolved in Distilled Water

The data for the solubility of quinhydrone up to 50° C.

are given in Table IV and the solubility curve in Figure 1. Luther and Leubner (*3*) give the solubility of quinhydrone

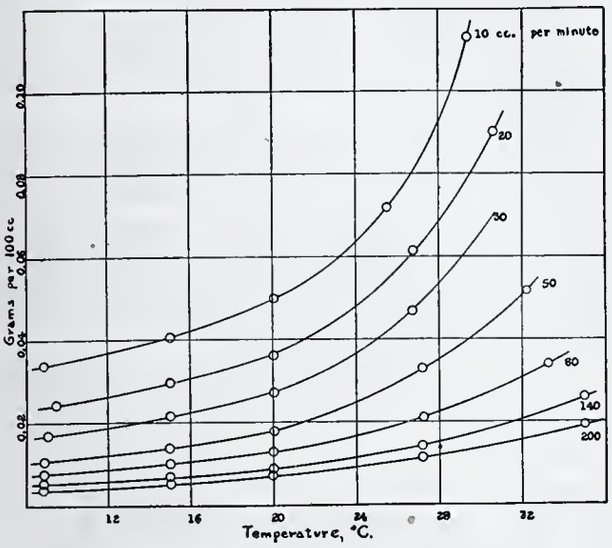


Figure 2—Variation of Quinhydrone Concentration in City Water Passed at Different Flow Rates and Temperatures through Tube Packed with Pellets of Quinhydrone

at 25° C., determined by an iodine titration, as 0.018 mole per liter. The present author obtained at the same temperature slightly less than 0.019 mole per liter.

Table IV—Solubility of Quinhydrone Dissolved in Distilled Water

Temperature	Quinhydrone in 100 cc. Soln.
° C.	*Gram*
0.3	0.116
6.0	0.122
8.4	0.156
10.0	0.154
15.0	0.245
20.1	0.320
21.0	0.321
30.2	0.530
30.9	0.542
40.5	0.754
50.0	1.035

Rate of Solubility of Pellets of Quinhydrone—The pellets of quinhydrone were $^9/_{16}$ inch (1.42 cm.) in diameter and $^1/_8$ inch (0.31 cm.) thick on the edge with convex faces making them $^1/_4$ inch (0.63 cm.) thick at the center. Each pellet had a weight of approximately 1 gram. They were manufactured in a tablet machine which insured uniformity. Before the pellets were used in the following tests they were retained in flowing water for 24 hours so that under test they would yield a more uniform rate of solubility. Forty of these pellets were retained in a tube $1^1/_8$ inch (2.85 cm.) in internal diameter and 3 inches (7.62 cm.) long. City water was allowed to percolate at various controlled rates and temperatures through them. The quinhydrone concentration in the effluent was determined by the above method.

The curves in Figures 2 and 3 depict the variation in concentration of quinhydrone dissolved from the pellets with a variation in the rate of flow and temperature of the water, and the per cent saturation of the resulting quinhydrone solutions at each condition.

Several interesting facts, some of which are apparent and not unexpected, are observed. The rate at which quinhydrone dissolved increased rapidly with a rise in temperature. Also the concentration of quinhydrone increased rapidly with a decrease in rate of flow. The per cent saturation of the solution with quinhydrone at each rate of flow decreased with an increase in temperature up to 21° C., from which temperature it increased at about the same rate it had decreased, the rate in each case being greater the smaller the rate of flow. However, the most noteworthy fact is that at approximately 100 cc. a minute and below 20° C. the concentration of quinhydrone was on the border line as to its ability to yield a reliable pH measurement, the minimum concentration as determined above being 7 mg. per 100 cc.

Again it is emphasized that these pellets were operated under ideal conditions. As the pellets dissolve, their surface decreases, and solids in industrial solutions will cover their surfaces, both conditions requiring frequent service to maintain the minimum operating concentration of quinhydrone in the test solution. It is also apparent that quinhydrone may easily be wasted.

In other words, none of the above-mentioned methods for the introduction of quinhydrone into the test solution which involves retaining the quinhydrone in the flowing stream is industrially satisfactory. It is also apparent that an apparatus which will add continuously to the flowing test solution the minimum amount of quinhydrone requisite for a pH measurement is the ideal method for introducing quinhydrone into the test solution. Such an apparatus will be described in a later communication.

Noble Metal Electrode

The function of the noble metal electrode in making a pH measurement with a quinhydrone electrode is to acquire accurately the potential of the oxidation-reduction equilibrium established in the solution by the dissolved quinhydrone, this potential being indicative of the pH of the solution. For an individual pH measurement where it is possible to clean the electrode before making a determination and to add quinhydrone much in excess of the above-determined minimum concentration, it matters little whether a gold, platinum, or a gold-plated platinum electrode is employed. However, in continuous pH work it is desirable to use an electrode which does not require frequent cleaning.

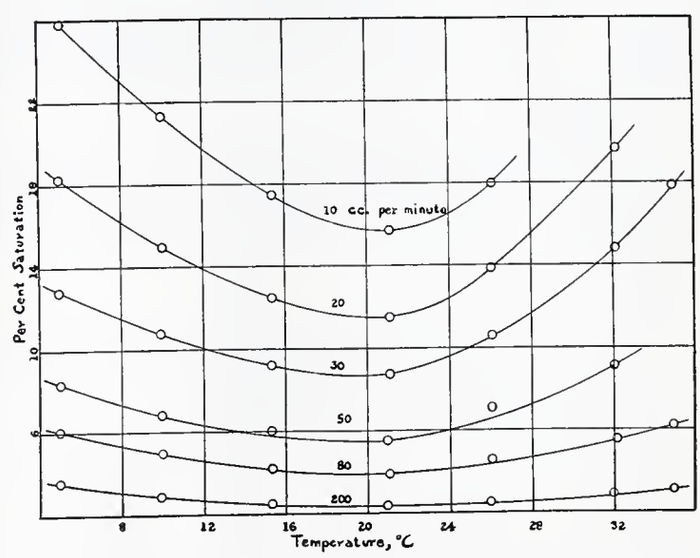


Figure 3—Variation in Saturation of Water Solution of Quinhydrone with City Water Passed at Different Flow Rates and Temperatures through Tube Packed with Pellets of Quinhydrone

During the progress of this work it was discovered that a gold electrode, after operating a few hours in some types of solutions, failed to acquire accurately the potential of the quinhydrone equilibrium reaction existing in the solution. This inaccuracy was detected by making individual pH measurements on the effluent from the flow channel in which was suspended the gold electrode. Subsequent experiments were conducted in order to correct this difficulty.

These experiments were made by using the continuous pH apparatus, a detailed discussion of which will be given in a later communication. Briefly, the apparatus consists

of a flow channel in which are suspended the noble metal electrode and a saturated calomel electrode. The test solution was passed through this flow channel after the requisite amount of quinhydrone had been added to it. The potential existing between the electrodes was automatically recorded by a Leeds and Northrup pH recorder having a paper speed of 4 inches (10.16 cm.) per hour. The potential of all dip-type pH measurements was obtained by a Leeds and Northrup portable potentiometer accurate to 0.5 millivolt.

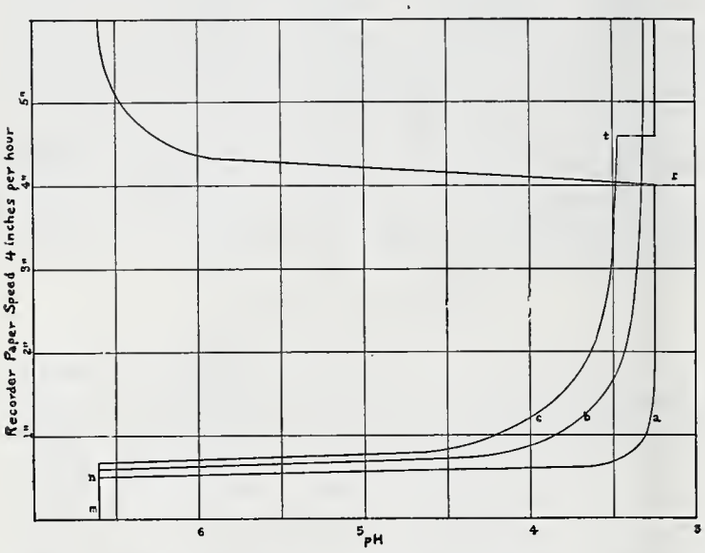


Figure 4—Increasing Unreliability of Gold Electrode for Continuous pH Measurements on City Water

Curve *a* obtained during first day of operation.
Curves *b* and *c* obtained after 2 and 3 days of continuous operation.

The test solutions that were passed through the flow channel for this experiment were either city water as it comes from the tap, or city water whose pH had been lowered by the addition of an acid, usually sulfuric acid. The latter test solution was made up and contained in a 30-gallon (113.5-liter) reservoir.

During the early stages in the operation of this continuous pH measuring apparatus, accurate results were obtained no matter how frequently the test solution in the flow channel was changed. Thus, curve *a*, Figure 4, is typical of these results. (The curves in Figures 4 and 5 were taken directly from the recorder paper.)

The curve *a*, Figure 4, will be explained. The pH of the tap water (6.6 pH) was recorded from *m* to *n*, at which point the tap water was turned off and the acid tap water turned into the flow channel. The pH fell rapidly to 3.24 pH and was accurately recorded as such. At *r* the acid tap water was turned off and the original tap water turned into the flow channel. The pH changed to its original value of 6.6 pH and was recorded as such.

After the flow channel had been operated for two days, the above procedure was repeated, resulting in curve *b*, Figure 4. Although the pH within the flow channel actually followed curve *a*, which was proved by checking the effluent with dip-type measurements, the recorded pH followed curve *b*. Even after an hour a stable reading was not obtained. When the acid tap water was exchanged for the original tap water, similar results ensued in that the correct pH was not registered. After 3 days' operation an identical series of events were carried out as depicted by curve *c*, Figure 4, the recorded pH being even more in error. However, it is interesting to note that at point *t* the gold electrode was removed and cleaned by placing it in 50 per cent nitric acid which was then brought to a boil. After a few minutes the electrode was removed, and washed in water and dilute ammonium hydroxide. Upon replacing the electrode, the correct pH value of 3.24 pH was almost immediately recorded. The cleaned electrode then operated satisfactorily for several hours, but eventually became increasingly insensitive for accurate pH measurements, yielding successively more inaccurate results similar to curves *b* and *c*, Figure 4.

The cause of a gold electrode's becoming increasingly insensitive is not known. It is thought to be connected with the presence of chlorine in the water. However, in this particular problem it was not so much the cause as the result which was of greater interest, since to eliminate the cause would probably require some type of purifying apparatus for the test solution. It was much simpler to change the gold electrode for one of platinum.

The cause of a gold electrode's increasing insensitiveness within a few hours' operation fortunately has no effect upon a platinum electrode. Similar tests were made with a platinum electrode as were conducted with the gold electrode. The results of these tests are given in curves *a*, *b*, and *c*, Figure 5. The platinum electrode retained its power of reproducibility after being operated for 6 days under the same conditions as caused the gold electrode to become increasingly insensitive after a few hours' operation. These tests were extended over periods of several months in an industrial installation on the same type of solution (Dalecarlia Filter Plant, Washington, D. C.). Although the platinum electrode lost its luster, its sensitivity was not impaired. Upon cleaning the electrode the indicated potential essentially remained unchanged.

Cleaning of Platinum Electrode

The usual methods of cleaning a gold electrode are not applicable to a platinum electrode to be used for continuous pH measurements in solutions which contain little more than the minimum concentration of quinhydrone to yield a sufficiently accurate pH measurement. The feasibility of a cleaning method was tested by checking the pH of the test solution in the flow channel, as indicated by the potential of the platinum electrode, against that of a gold electrode used in a dip-type measurement on a portion of the effluent from the flow channel, to which portion was added more quinhydrone. Several different cleaning methods involving boiling acids or alkalies were tried with variable degrees of success—that is, upon placing the cleaned platinum electrode in the flow channel, the recorded pH values were of variable degrees of accuracy and stability. Usually a drift in potential occurred, tending toward the correct potential.

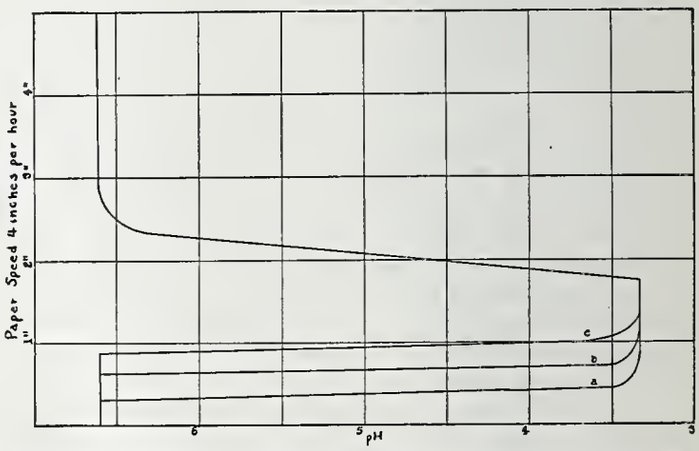


Figure 5—Ability of Platinum Electrode to Indicate Accurately Correct Potential in Continuous Quinhydrone pH Measurements

Curve *a* obtained during first day of operation.
Curves *b* and *c* obtained after 3 and 6 days of operation.

A cleaning method was finally discovered which permits the platinum electrode to indicate accurately the correct potential within 2 to 5 minutes. (In any electrometric pH measurement a variable amount of time is always necessary for the establishment of equilibria conditions.) The method of cleaning the platinum electrode consists in boiling the electrode in a 5 to 10 per cent sodium bisulfite solution for at least 3 minutes. The electrode is removed, washed in water, and inserted into the flow channel. Care must be taken not to touch the electrode or contaminate it in any way.

Obviously such a cleaning will not remove many things that deposit on the electrode from industrial solutions. Therefore, in cleaning an electrode that has been contaminated, it is better to boil the electrode until it becomes bright in 50 per cent nitric acid, followed by a water wash. But it is absolutely essential to follow this acid treatment by boiling the electrode in the 5 to 10 per cent sodium bisulfite solution.

The thoroughness of terminating the cleaning of a platinum electrode with the sodium bisulfite treatment was further demonstrated with a battery of five flow channels operating in parallel on the same solution. The five platinum electrodes were cleaned by this new method and each inserted into a flow channel. Within a few minutes every electrode was indicating the correct pH within 2 millivolts. This experiment was repeated several times to show that the results were not accidental.

Literature Cited

(1) Biilman and Jensen, *Bull. soc. chim.*, **41**, 151 (1927).

(2) Clarke, "The Determination of Hydrogen Ions," 3rd ed., p. 205, Williams & Wilkins, 1928.

(3) Luther and Leubner, *J. prakt. Chem.*, **35**, 314 (1912); *Z. anorg. Chem.*, **74**, 389 (1912).

Ignition Losses in Potash Analyses of Triple Superphosphate Mixtures[1]

L. B. Lockhart

Tennessee Copper & Chemical Corp., Atlanta, Ga.

FOR several years it has been known that fertilizer mixtures containing potash salts and superphosphate may give erratic results, usually low, upon analysis for potash content by the Official Method. A number of papers have appeared on this subject from 1925 to date, the difficulties being usually ascribed to the presence of phosphoric acid or its salts which are present in the solution used for evaporation and ignition. Various methods for removal of phosphates have been proposed (*1*).

Kerr (*6*) found that where a small quantity of phosphoric acid was present in the potash solution, the potash results were from 0.2 to 0.3 per cent too low. Bible (*2*) found low results with silica dishes, especially with "treble" superphosphate mixtures. Some of his results in porcelain were 30 per cent too low, with low results also in platinum. Haigh (*4*), using the Official Method without removing phosphates, obtained losses as high as 36 per cent of the true potash content with fertilizer mixtures containing up to 16 per cent of phosphoric acid and 4 to 5 per cent of potash. Satisfactory checks were not obtained. In a special study of the effect of silica dishes, Haigh (*3*, *5*) found low results as compared with ignition in platinum dishes.

The present paper deals primarily with the temperature of ignition. None of the papers referred to states the time, temperature, or method of ignition. The Official Method (*1*) states: "Maintain a full red heat until the residue is perfectly white." This temperature may be between 600° and 900° C. With no precautions indicated as to the effect of excessive temperatures, the higher temperatures are often used.

The samples used were commercial mixtures of superphosphates, potash salts, and in most cases mineral and organic ammoniates. The procedure was to prepare the solution by the Official Method, using 2.425 grams of the fertilizer, making to 250 cc., and taking a 40-cc. aliquot for evaporation. A smaller aliquot was used for samples of high potash content. Thus the size of the aliquot represented a somewhat smaller sample than specified in the Official Method. Silica dishes 4 inches (10.16 cm.) in diameter and with flat bottoms were used, except where platinum is designated. These dishes were in regular use and in good condition. For each comparison, aliquots were taken from the same flask so that variations in making up the solution would not affect the re-

[1] Received September 26, 1930. Presented before the Division of Fertilizer Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Table I—Comparative Potash Results under Different Ignition Conditions

Kind of Fertilizer	P_2O_5 in Aliquot	Potassium Chloroplatinate	Heat of Ignition	Ignition Period
	Gram	*Gram*		*Min.*
4–24–12	0.0438	0.2750	Very faint red, Cone 022 (590° C.)	3
		0.2764	Dark cherry red, Cone 014 (830° C.)	5
		0.2752[a]	Dark cherry red	5
		0.2724	Very bright cherry, Cone 012 (890° C.)	5
4–24–12	0.0232	0.1200	Low red	3
		0.1178	Bright cherry red	3
4–24–12	....	0.1180	Lowest red	2
		0.1170		
		0.1092	Full red	10
0–24–24	0.0242	0.2344	Lowest red	3
		0.2350	Dark cherry red	4
		0.2282	Bright cherry red, Cone 011 (920° C.)	3
		0.2326[a]	Bright cherry red	4
		0.2326	Full cherry red, no H_2SO_4 added	4
		0.2338	Lowest red, no H_2SO_4 added	4
0–24–24	....	0.1175	Lowest red	2
		0.1170		
		0.1157	Bright red	10
4–24–4	0.0511	0.0922	Lowest red	3
		0.0904	Bright cherry red	4
		0.0892[a]	Bright cherry red	4
2–14–4	0.0050	0.0810	Lowest red	4
		0.0772	Bright cherry red	10
2–12–6	0.0064	0.1222	Lowest red	4
		0.1166	Bright cherry red	10
2–10–4	....	0.0852	Lowest red	2
		0.0802	Full red	10
Laboratory sample: KCl + 85% H_3PO_4	0.2640	0.1246	Just below white (above 900° C.)	2
		0.0060[b]		
		0.1306		
		0.1084	Just below white (above 900° C.)	8
		0.0203[b]		
		0.1287		
		0.1114	Just below white (above 900° C.)	13
		0.0202[b]		
		0.1316		

[a] Ignited in platinum.

[b] Additional potash found in silica dishes by boiling with hydrochloric acid. Dishes used were badly damaged, and from 25 to 29 mg. of silicon dioxide were present with the potassium chloroplatinate precipitate.

sult. In transferring the ignited residue from silica to porcelain, the solution was not filtered, but the potassium chloroplatinate was dissolved in hot water after weighing, so that the net weight was obtained.

The aliquots were evaporated on the water bath, fumed off over Gilmer heaters at a low temperature, and then placed in the electric furnace at the temperature and for the period stated. It was found that 2 minutes in the electric furnace removed practically all of the ammonia, when various types of dishes were used. Even where the lowest visible red heat was used for 2 minutes only, the maximum amount of ammonia found was 0.2 mg. It may be noted that the Alternative Method (*1*) for potash specifies: "Ignite over a free flame below a red heat until all volatile matter is driven off."

Early in these determinations it was noted that after ignition small amounts of potash might sometimes be left undissolved in the silica dishes. Unusual care was used in dissolving the ignited residue, particularly in regard to the time. All of the dishes were tested for potash by boiling out with hydrochloric acid, and amounts of potash varying from none to 0.4 mg. of potassium chloroplatinate were found. These amounts were included with the amounts reported. In one case where a high temperature was used, 1.0 mg. of potassium chloroplatinate was noted. The ignited residue, although somewhat slow in dissolving, can be readily dissolved in a reasonable time, especially if the ignition has been made at a low temperature. Five minutes were found to be ample for solution before transferring to porcelain.

In ignition where phosphates are present, the phosphoric acid may replace in part the sulfuric acid which is more volatile at high temperatures. Low-temperature ignition prolongs the life of silica dishes and reduces the amount of silica loosened from the dishes. In this series of analyses, the maximum amount of silica noted in the precipitated potash was 3.2 mg. where a high temperature was used with triple superphosphate mixtures. The usual amount of silica varied, with low-temperature ignition, from none to 0.4 mg. Dishes deteriorate more rapidly with triple superphosphate mixtures. All mixtures containing acidulated phosphates normally contain phosphates in the potash solution.

Ignition residues containing triple superphosphate melt at a very low temperature, forming a glassy instead of a crystalline or granular residue. Although few duplicate analyses are shown, no exception to low results with high-temperature ignition was obtained. As the only object of ignition is to remove ammonia and organic matter, the results with low-temperature ignition are probably nearest the true potash content.

It is suggested that low-temperature ignition be stressed in any future study of potash methods for mixed fertilizers, and that adequate time be given for complete solution of the ignited residue.

Literature Cited

(1) Assocn. Official Agr. Chem., Methods, p. 15 (1925); also references cited below.
(2) Bible, C. M., *J. Assocn. Official Agr. Chem.*, **8**, 420–3 (1925).
(3) Fraps, G. S., *Ibid.*, **9**, 192 (1926).
(4) Haigh, L. D., *Ibid.*, **10**, 220–3 (1927).
(5) Haigh, L. D., *Ibid.*, **11**, 219–20 (1928).
(6) Kerr, A. P., *Ibid.*, **8**, 419–20 (1925).

Practical Methods of Detecting and Estimating Methyl Chloride in Air and Foods

With a Description of a Modified Combustion Method[1]

Mathew J. Martinek and Wm. C. Marti

Bureau of Laboratories and Research, Chicago Department of Health, Chicago, Ill.

Comparative studies of available field tests for methyl chloride in air showed the copper gauze–flame test to be the most efficient and rapid.

A study of laboratory methods for the qualitative detection of methyl chloride in miscellaneous samples resulted in developing a practical combustion method which proved satisfactory. It is sensitive to about 50 parts of methyl chloride per million parts of air.

For quantitative work, a modified combustion method was devised in which the methyl chloride gas, diluted with air, is oxidized, and the halogen products of combustion—i. e., the hydrochloric acid gas and the free chlorine and its oxides—are absorbed in a solution of sodium carbonate and arsenious acid. The resultant chlorides are precipitated with silver nitrate and titrated by a very sensitive modified Volhard method, the accuracy of the method being about 50 parts per million. It is applicable to various types of samples, including air, food materials, urine, etc.

THE recent occurrence of poisonings and fatalities from methyl chloride gas used in mechanical refrigerating systems in Chicago (*2*) made it necessary to seek practical tests for the rapid detection of this gas and to develop and perfect accurate quantitative methods for its estimation in air and miscellaneous substances.

In this report the subject will be treated under two headings, field methods and laboratory methods, with special attention to the development of a modified combustion method.

Field Methods

A method commonly used by service men for detection of gas leaking from refrigerating systems is to coat the pipes with a film of soap, using a shaving brush and shaving stick to produce a lather. Wherever a leak occurs there will be a formation of bubbles. This test is useful but is not suitable for detecting leaks in inaccessible places. In refrigerating systems containing a mixture of methyl chloride and sulfur dioxide, the test used is to pass an open bottle of ammonium hydroxide along the pipes, the formation of a white cloud indicating a leak. In small concentrations where the gas cannot be detected by odor, the copper flame test for organic halogens was found to be the most sensitive and convenient.

The following apparatus has been adopted as an official field test by the Inspection Bureau of the Chicago Department of Health: A small alcohol lamp (Figure 1), fitted with a cone of copper gauze, is constructed as follows: A wide-

[1] Received May 25, 1931.

mouth bottle, *A*, is stoppered with a cork, *B*, through which is inserted a glass tube, *C*, for holding a wick, *F*. Over this is suspended a copper gauze cone, *E*, held in place by a wire support, *D*.

For operation the lamp is partially filled with alcohol and the wick ignited. Ordinarily the lamp will burn with a pale blue flame but, if brought into the presence of organic halides, it burns with a distinct blue-green flame. The test is sensitive to about one part per 100,000. The lamp should not be used where large quantities of the gas might be present. The lower limit of flammability is 8.1 per cent of the gas to 91.9 per cent of air by volume (*3*).

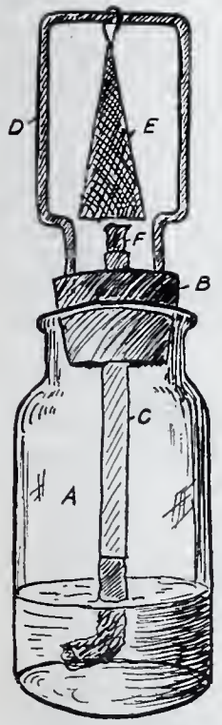


Figure 1—Lamp Used in Official Test of Chicago Department of Health

Laboratory Methods

The detection of methyl chloride by dissolving it in water and then refluxing it with freshly precipitated silver oxide in order to convert it to silver chloride was tried and found unsatisfactory.

Hydrolysis of the methyl chloride to form methanol by use of strong alkali or potassium acetate with alkali also proved unsuccessful unless boiled for a very long time under high pressure. Hydrolysis and oxidation of the methyl chloride to formaldehyde, and then testing for the latter by Rimini's method (*1*), likewise proved unsuccessful because the formaldehyde could never be produced in the low concentrations handled.

The method of Roka and Fuchs (*4*), in which methyl chloride dissolved in alcohol is heated with potassium iodide in a sealed tube for 3 or 4 hours at 60° C. and the resultant methyl iodide distilled and precipitated as silver iodide, was also discarded since the reaction was not sensitive to minute amounts of methyl chloride.

After these failures, a combustion method was devised based on the oxidation of methyl chloride in the presence of a large excess of air, according to the following equation:

$$2CH_3Cl + 3O_2 = 2CO_2 + 2H_2O + 2HCl$$

This reaction is not exactly correct as it has been shown later that chlorine and oxides of chlorine are also formed. The resultant hydrochloric acid gas is absorbed in a 2 per cent silver nitrate solution. The presence of methyl chloride is indicated by a cloudy precipitate of silver chloride.

The apparatus used in making this test consists of an electric furnace through which passes a quartz combustion tube whose outlet is connected to an absorption bottle containing the silver nitrate solution. For testing air samples, the furnace is heated to approximately 1000° C., and the inlet end of the tube is connected to a 200-cc. Thoerner gas-sampling bottle placed in a vessel of mercury. The gas is passed through the furnace by displacement and by suction applied at the outlet end. To exclude chlorides or free hydrochloric acid, which may be present in the air used for flushing out the sample, a soda-lime tube and cotton filter are introduced. A distinct precipitate of silver chloride was formed in samples containing 50 parts of methyl chloride per million parts of air. The test is sensitive to all organic halogens, and therefore the source of the sample should be known before any conclusion is reached as to the presence of methyl chloride.

The above combustion method for qualitative tests was used as a basis for a quantitative method, suitable modifications being made to assure sufficient accuracy. The specifications of the apparatus (Figure 2) are as follows: A 4-foot (10.16-cm.) quartz tube, *A*, having an inside diameter of 1/4 inch (0.63 cm.), is inserted through two Hoskins electric furnaces in series, *B* and *B′*, the temperature of which is regulated by means of two resistance units, *C* and *C′*. The inlet end of the tube is connected to a measuring pipet, in which methyl chloride for analysis is placed. This pipet is connected to a tower containing soda lime and a cotton filter to free the air entering the apparatus from chlorides. The outlet end of the combustion tube is connected to two absorption bottles, *F*, arranged in series, having an outlet tube of fritted glass with pores measuring 100 to 120 microns. This arrangement breaks the gas up into very fine bubbles and assures very good absorption. These bottles are connected to a gas meter, *G* (wet type), which serves as a means of measuring the volume of air used and of regulating the rate of flow. The air is drawn through the apparatus by means of an electric vacuum pump, but other suction apparatus may be used.

Cylinders containing a good grade of commercial methyl chloride manufactured by the Roessler & Hasslacher Chemical Company and obtained in the open market were used in developing the method. This grade of methyl chloride was analyzed in the laboratories of the National Board of Fire Underwriters, and had a purity of 99.6 per cent and a water content not over 0.026 per cent (*3*). The gas before use was dried over soda lime and Dehydrite, and all precautions, such as drying the mercury surface and the buret, were used to ensure a dry sample. Stopcock grease recommended by the Bureau of Standards was used (*5*).

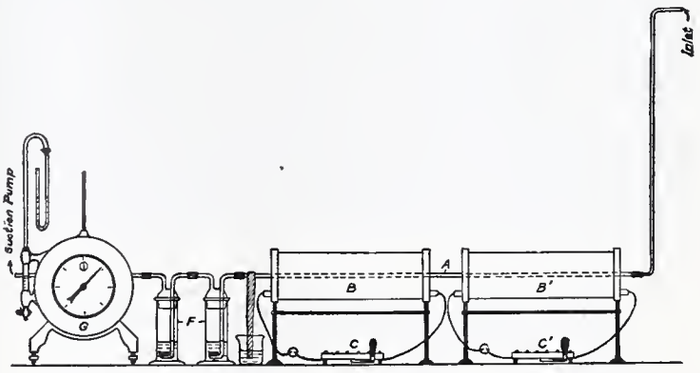


Figure 2—Apparatus for Combustion Method

For measuring the methyl chloride accurately an all-glass microburet of 5 cc. capacity and calibrated to 0.01 cc. was constructed (Figure 3). It is connected to a compensator, *A*, and the whole is immersed in a water jacket. The remaining outlet of the three-way stopcock, *B′*, is fused to a glass dilution chamber, *D*. This chamber has two tubes, *E* and *E′*, fused into it, tube *E* leading from the top of the chamber, and tube *E′* reaching to the bottom. Stopcock *B* is a three-way stopcock, one opening of which is connected, by means of tube *C*, to the outside air. The buret is operated in the following manner: The gas is adjusted on both sides of the mercury in the compensator manometer to atmospheric pressure by opening the manometer cock, *F*, and removing the lower buret cock plug, *B′*. Plug *B′* is replaced, manometer cock *F* is closed, and the top of the mercury meniscus is marked in the manometer tube. Lower buret cock *B′* is turned away from compensator, and stopcock *B* is opened through *C*. Buret leveling bulb *G* is raised until the mercury is at *C*. The sample is connected at *C*, and about 5 cc. are drawn in by lowering the leveling bulb *G*.

This gas is discharged into the outer air in order to avoid contamination of the laboratory air. This should be repeated several times. Next approximately 5 cc. of sample are drawn into the buret and cocks B and B' are closed. With the leveling bulb so adjusted on the ring support that the mercury in the bulb is approximately level with the mercury in the buret, lower buret cock B' is turned to communicate with the compensator. If the gas sample is not at atmospheric pressure, the mercury will rise or fall in the compensator manometer. The buret leveling bulb should be raised or lowered carefully until the mercury in the manometer is brought back exactly to the mark, and then the lower buret cock should be turned away from the compensator. The gas sample in the buret is now at atmospheric pressure, and the volume can be read. Barometric pressure and temperature of the water in the jacket are noted. All volumes are calculated to standard conditions of 760 mm. and 0° C. The buret is then connected to the combustion train at E and to the drying tower at E'.

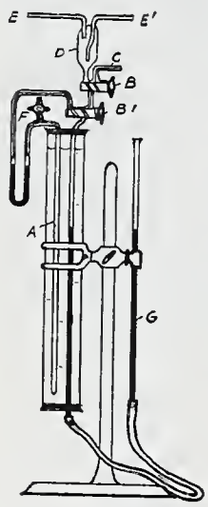


Figure 3—Microburet for Measuring Methyl Chloride Accurately

The temperature of the furnaces is allowed to reach about 1000° C., and the absorption bottles, F, containing 25 cc. of 0.005 N silver nitrate, are attached. Suction is started and so regulated that the meter registers $^1/_2$ cu. ft. (0.014 cu. m.) of air per hour. By raising the leveling bulb G, opening B and partially opening B' to communicate with chamber D, the sample is very slowly passed into the chamber, where it is constantly diluted with dry air before it enters the furnaces. After 1 hour, the absorption bottles are disconnected, and the silver chloride filtered off through a Gooch crucible. The precipitate is washed with small amounts of distilled water and the filtrate acidified with nitric acid and titrated with 0.005 N sulfocyanate, using ferric ammonium sulfate as indicator, according to Volhard's method (*6*). The results obtained are shown in Table I, and were too low to be satisfactory.

Table I—Results with Silver Nitrate Used as Absorbent

Gas Used		Gas Recovered	Error
Cc.	*Gram*	*Gram*	*%*
4.92	0.00982	0.00930	5.2
4.47	0.00893	0.00822	8.0
4.18	0.00840	0.00759	9.6
4.84	0.00966	0.00930	3.7
4.76	0.00907	0.00871	3.8

At this stage of the experiment, tests indicated that either all the methyl chloride had not been changed to hydrochloric acid, that the acid was not completely absorbed by the silver nitrate, or that free chlorine or oxides of chlorine were being formed. By repeating the combustion and passing the gases of combustion into a solution of starch and cadmium iodide, the development of a blue color indicated the presence of free chlorine or oxides of chlorine. Substitution of a solution of sodium hydroxide did not remedy the trouble. This necessitated the use of reducing agents strong enough to change the chlorine and its oxides to hydrochloric acid. After trying several possibilities, an alkaline solution of sodium arsenite was found to give satisfactory quantitative results. This solution was made by dissolving 0.2 gram of arsenious oxide in 100 cc. of a 1.0 per cent solution of sodium carbonate.

The best results are obtained by using the following procedure: The gases of combustion are absorbed in two fritted-glass absorption bottles, each of which contains 20 cc. of the alkaline sodium arsenite solution. After 1 hour, the absorption bottles are removed, and the contents washed into a 100-cc. volumetric flask to which 5 cc. of 3 to 1 nitric acid have been added. Twenty-five cubic centimeters of standard 0.1 N silver nitrate are added, and the whole is diluted to the 100-cc. mark. The flask is stoppered, well shaken, and the precipitate allowed to settle. An aliquot portion (25 cc.) of the filtered solution is titrated with 0.05 N potassium sulfocyanate, using a 5-cc. microburet capable of delivering a 0.01-cc. drop. A crystal of ferric ammonium sulfate is used as indicator instead of the saturated solution. By this method a sharp end point results, and the volume of the solution titrated in no case exceeds 40 cc., whereas in the earlier method the volume amounted to as much as 300 cc. Table II shows some of the values obtained. The largest error did not exceed 0.5 per cent, and the test proved sensitive to 50 parts of methyl chloride in one million of air. By the use of a platinum needle attached to the microburet, making it possible to split drops, the accuracy of the titration was greatly enhanced.

Table II—Results with Arsenious Oxide and Sodium Carbonate Used as Absorbent

Gas Used		Gas Recovered	Error
Cc.	*Gram*	*Gram*	*%*
4.65	0.00878	0.00879	0.1
4.77	0.00901	0.00898	0.4
4.70	0.00880	0.00884	0.4
4.47	0.00857	0.00853	0.4
4.96	0.00977	0.00973	0.4
4.95	0.00969	0.00967	0.2
4.96	0.00970	0.00965	0.5

For routine testing, the procedure is as follows: The sample is collected in a 200-cc. Thoerner gas-sampling bottle by mercury displacement. One opening of the bottle is connected to the inlet end of the combustion train, and the sample is slowly passed into the heated furnace tube, displacing the sample in the Thoerner bottle with mercury. The train is then cleared with chloride-free air, this air being passed through at the rate of $^1/_2$ cu. ft. (0.014 cu. m.) per hour. After 1 hour, the absorption bottles are removed, the titration is performed as stated in the previous paragraph, and the amount of methyl chloride present is calculated from the chlorides found by the titration.

For the determination of the methyl chloride in a sample of foodstuffs, urine, or similar material, the sample is placed in an Erlenmeyer flask equipped with a two-hole rubber stopper covered with tin foil. Glass tubes pass through these holes, the inlet tube passing to the bottom of the flask and the outlet tube passing through only to the bottom of the stopper. This flask is immersed in a hot-water bath, and air is drawn through the warmed sample. This air is very slowly passed through the combustion train at the same rate as for the test on air samples. From the amount of chlorides found the quantity of methyl chloride in the sample is calculated. Blank tests were run on the sample by passing the air from the heated flask directly into the alkaline arsenite solution, thus determining any free hydrochloric acid or chlorine in the sample.

Literature Cited

(1) Allen, "Commercial Organic Analysis," 5th ed., Vol. I, p. 327, Blakiston, 1930.
(2) Kegel, McNally, and Pope, *J. Am. Med. Assocn.*, **93**, 353–8 (1929).
(3) National Board of Fire Underwriters, *Bull.* **1418**, 25 (August 26, 1926).
(4) Roka and Fuchs, *Z. anorg. Chem.*, **71**, 381 (1927).
(5) Shepherd, *Bur. of Standards Res. Paper* **226**, 142 (1931).
(6) Sutton, "Volumetric Analysis," 11th ed., p. 150, Blakiston, 1924.

Thiosulfate Titrations of Small Amounts of Iron in Glass Sands[1]

Lewis B. Skinner

First National Bank Building, Denver, Colo.

A description of a rapid and accurate method for iron determination, using ordinary laboratory equipment, is given.

Sand low in alumina is run to dryness with hydrofluoric acid in a silver dish; the residue is fused a few moments with sodium hydroxide and chlorate; the melt is disintegrated by water and transferred to a beaker; the solution is acidified by hydrochloric acid and a little nitric and boiled; ferric hydroxide is precipitated by an excess of ammonia, filtered off, and dissolved in a little dilute hydrochloric acid; the solution is evaporated to a small volume, potassium iodide and starch are added, and it is titrated by a standard thiosulfate.

When alumina is high relatively, sodium chlorate is omitted in the fusion, the melt is disintegrated in water, sodium sulfide is added, the sulfide of iron is filtered off, dissolved, and oxidized, and ferric hydroxide is precipitated by ammonia and is treated further as shown above.

In trying various procedures for the commercial removal of iron from glass sand, it was found that published methods for the determination of iron oxide on this material (*1*, *3*) and any gravimetric ones which could be devised were too tedious, so it was decided to attempt to work up a volumetric scheme not demanding complicated equipment and manipulations. All investigatory work done will not be detailed for the list of experiments would be too long, but some items will be noted.

Numerous titrations at various temperatures by stannous chloride, using potassium thiocyanate as an internal indicator in a ferric chloride solution, were made. The action on small amounts of ferric chloride by cold stannous chloride proved too sluggish and indefinite, so boiling throughout the period of titration was done. This affected the thiocyanate so as to provide widely varying end points.

Attempts to compare quantitatively the colors produced by ferric sulfocyanate in mixtures of amylic alcohol and ether were not successful on material of this kind, owing to the extraordinary care required to avoid contamination, the delicate manipulation found necessary, and the magnification by the dilutions required of variations in small-quantity weighings, separations, and measurings.

Portions of weak ferric chloride solutions containing free hydrochloric acid, to each of which 150 mg. of potassium iodide were added, were titrated cold by a weak standard solution of sodium thiosulfate, adding starch solution near the finish. Although this amount of iodine would seem excessive, it was found to be insufficient for rapid titrations, and therefore trials of various greater quantities were made. Excesses over 600 mg. for each titration did not prove beneficial. However, provided sufficient potassium iodide is added, additional amounts do not affect final end points.

Varying the volumes of solutions being titrated by greater or lesser amounts of the standard thiosulfate, due to higher and lower irons, likewise does not affect titrations, except to prolong the time of titration at greater dilutions.

Upon allowing a weak unprotected thiosulfate solution to stand, it was found that it decomposed quite rapidly, requiring almost daily standardization. Neither sodium hydroxide nor sodium carbonate proved effective as preventatives.

Yoshida (*4*) recommends the use of either carbon disulfide, disodium phosphate, or borax for sterilizing this solution against bacterial action which causes its decomposition into sulfate and sulfur.

Carbon disulfide does not protect the weak thiosulfate solution required. Disodium phosphate (7 grams of Na_2HPO_4 per liter) gives an end point which is far too slow in developing. Borax (19 grams of $Na_2B_2O_7.10H_2O$ per liter) protects the solution, but requires too much time to discharge eventually the color which returns a number of times. Benzoate of soda (7 grams per liter) permits of splendid titrations, but does not protect the thiosulfate solution effectively. Boric acid (10 grams per liter) protects the solution, but causes long-drawn-out end points. Benzoic acid (2.5 grams per liter) furnishes rapid and accurate end points and preserves the solution fairly well and may be used. Boric acid (5 grams per liter) protects the solution better than benzoic acid, but is a little more tedious in securing final end points. Lundell, in a private communication to the author, suggested sterilizing. This was done by boiling a solution of the desired quantity of thiosulfate for about 1 hour, cooling, diluting to the required volume, using freshly boiled water, and putting this into a glass stoppered bottle which had been treated by hydrochloric acid and washed by boiled water. This solution seems to keep quite well without the necessity for special precautions in handling.

To determine the effect of the presence of variable amounts of hydrochloric acid, titrations were made on weak acidified ferric chloride solution by a thiosulfate solution, with the results as shown in Table I.

Table I—Effect of Variable Amounts of Hydrochloric Acid in Protecting Thiosulfate Solution

Std. $FeCl_3$ Taken	HCl (Sp. Gr. 1.18) Present	Std. Thiosulfate Required	Std. Thiosulfate Required for HCl without $FeCl_3$ Added
Ml.	*Ml.*	*Ml.*	*Ml.*
0.1	0.002	0.15	..
0.1	1	0.25	..
5.0	0.002	4.65	..
5.0	1	4.85	0.10
5.0	2	4.95	0.10
5.0	3	5.00	0.15
5.0	4	5.10	0.20
5.0	5	5.20	0.25

In these titrations, the greater the amount of acid present the longer the time required to reach an end point eventually. The larger quantities of hydrochloric acid added provide more straw color at the finish.

Since there is a necessity for having some free hydrochloric acid present, it was decided to add 1 ml. (1.18 grams) for all subsequent titrations, the varying amounts of iron in unknown determinations taking up such a small proportion of the 1 ml. as to be of no moment. Since blanks will be run, the effect of the hydrochloric used will be accounted for anyway.

Preparation of Solutions Used

Potassium Iodide Solution—Dissolve 120 grams of potassium iodide in water and dilute to 200 ml.

[1] Received March 31, 1931.

Starch Solution—Low (*2*) recommends the following:

Make a cold saturated solution of commercial sodium chloride in distilled water and filter it. To 500 ml. of this solution add 100 ml. of glacial acetic acid and 3 grams of starch. Mix cold. Boil until nearly clear, about 2 minutes. Add a little water to replace that lost by boiling, perhaps 25 ml. A true solution of all the starch is thus obtained. No filtering or settling is required, and the solution may be cooled and used at once. It keeps indefinitely and gives sharper end points than the ordinary starch liquor.

Believing it advisable to adhere to standardized conditions, it is felt that pipetting 1 ml. of this solution into each determination is preferred to using varied quantities of starch solution prepared from time to time.

Standard Thiosulfate Solution—Dissolve 1.55 grams of c. p. sodium thiosulfate ($Na_2S_2O_3.5H_2O$) crystals in distilled water and dilute to 1 liter, preserving the solution by sterilizing as described.

To standardize, accurately weigh on a gold button balance sensitive to 0.01 mg., portions of 15 to 16 mg. of thoroughly cleaned iron wire into 150-ml. beakers.

An analytical balance does not weigh closely enough to depend upon two or three 15- to 16-mg. portions for standardizing, so an accurately measured 10-inch (25.4-cm.) length of No. 30 gage iron wire may be weighed thereon and be cut precisely into five parts 2 inches (5.08 cm.) long and each treated as noted in the following. This will prove more accurate usually than taking aliquot parts of a dilute solution of iron chloride. The portions will not check so closely between themselves as will those weighed on a button balance, but should be closer than those from separate weighings on an analytical scale, even though done accumulatively.

Cover each beaker with a watchglass; dissolve in 2 or 3 ml. of 1 to 3 nitric acid; boil out nitrous fumes; add a couple of small crystals of chlorate to destroy carbonaceous matter; continue heating a minute; dilute to about 100 ml.; add ammonia in excess; bring to a boil; filter on a 9-cm. paper; wash the precipitate five times by hot water to remove nitrates; discard the filtrate; remove the bulk of the ferric hydroxide from the paper into a 180-ml. "copper" flask by a wash-bottle jet; place the flask beneath the funnel and paper formerly containing the precipitate; dissolve the hydroxide remaining on the paper by means of a hot mixture of exactly 1 ml. of strong hydrochloric acid and 5 to 10 ml. of water; and wash the paper free from ferric chloride. Look for iron behind the fold.

Avoid allowing the ferric nitrate solution to go to dryness and thereby decompose the compound (shown by red nitrous fumes), but should this happen, take up with nitric acid, (not hydrochloric acid), and note whether or not all the residue is dissolved.

Swirl the contents of the copper flask so as to wash down all the hydroxide into the solution, and boil down to about 10 ml., this concentration being advisable for taking specks into solution.

Sometimes such baked-on specks escape observation and are only noted when titrations are approaching completion, in which case, pour the solution into another flask, add 0.1 to 0.2 ml. of strong hydrochloric acid to the original flask, run the few drops of acid around the wet surfaces of the glass onto the spots while heating gently, return the original solution and complete the titration.

Cool the flask and contents, wash down the sides, pipet 1 ml. of potassium iodide solution into the liquid, and, to avoid air-oxidation, pass carbon dioxide gas from a limestone and commercial muriatic acid generator through a sodium bicarbonate solution wash bottle at a minimum rate of four bubbles per second.

The glass tube conveying the gas into the titration flask should be bent at the upper portion to hook on the rim and at the lower portion to conform to the inner wall. It should terminate below the bulge of the flask. The gas is so heavy that it is not necessary to stopper the flask or to pass the gas through the solution in it while titrating.

While the contents of the flask are being swirled, deliver the standard thiosulfate solution from a 50-ml. buret until the yellow color is almost discharged, pipet 1 ml. of starch solution into the flask, wash down the sides, and continue the titration until the solution is colorless. The color may return several times when handling relatively high irons, but should be discharged from time to time by further additions of drops of thiosulfate, or until the solution remains colorless for some 15 minutes.

Since the solution is protected from oxidation by carbon dioxide gas, it makes little difference how long a time is taken to remove all color eventually.

Ground glass stoppered burets are not convenient and are liable to breakage, it being advisable to have the buret tip deliver below the neck of the flask. Clamps on rubber tubing should not be used, because of variations of pressure on the rubber and possible changes of position. Glass rod plugs, about $^5/_{16}$ inch (0.79 cm.) long, inserted in the rubber coupling between the buret and the glass tip, work admirably and accurately when not shifted by squeezing to permit flow of the liquid.

Titrations should be conducted over white paper or other white surfaces and be placed between the observer and a window.

The colors produced by iodide of starch range, as free iodine is removed, from greenish black to blue, to purple, to pink, and to straw. When the straw stage is reached and the titration is allowed to stand for a minute or so, the color usually changes back to pink. In any event, a reading should be taken at this point and a drop or so of the solution added to determine whether the straw-colored solution may be bleached to one which is colorless.

For a blank, place the same volumes of water, hydrochloric acid, and potassium iodide and starch solutions in a flask, and discharge the color by the thiosulfate. Between 0.1 and 0.2 ml. may be required, which may be deducted from the preceding.

Multiply the iron taken by its percentage of purity and by 1.4298, and divide by the net milliliters used. The thiosulfate solution should be equivalent to about 0.0005 gram of Fe_2O_3 per milliliter.

Pinkish or bluish colored flasks tend to mislead an analyst and should not be used.

Sodium Hydroxide Solution—Dissolve 500 grams of fresh, dry, fused c. p. caustic soda (NaOH) in distilled water and dilute to 1 liter. Do not store this in unprotected glass bottles since it will attack the glass. Ceresin-coated glass bottles are recommended.

Sodium Sulfide Solution—Dissolve 200 grams of fresh c. p. sodium sulfide ($Na_2S{\cdot}9H_2O$) in distilled water and dilute to 1 liter.

Sodium Sulfide Wash Water—Dissolve 5 grams of $Na_2S{\cdot}9H_2O$ in 1 liter of water.

Sodium Chlorate Solution—Dissolve 50 grams of $NaClO_3$ in 1 liter of water.

Method for Sands Low in Alumina

(Sands containing approximately 0.25 per cent aluminum oxide.)

Blanks should be run, measuring the liquid constituents carefully and weighing the solids. The aggregate of the iron in the reagents used is sufficient to vitiate results.

(*a*) Weigh 10 grams of 100-mesh glass sand into a 250-ml. silver dish.

(*b*) Add 75 ml. of 48 per cent C. P. hydrofluoric acid (no sulfuric), and evaporate to dryness.

(*c*) Cool, add 10 ml. of sodium hydroxide solution and 1 ml. of sodium chlorate solution, run the mixture around the sides of the dish, and evaporate to dryness.

(*d*) Heat over a flame to incipient redness in order to cause quiet fusion, and run the mass slowly around the sides of the dish while still being heated. Do not stop heating when effervescence, due to dehydration, ceases.

(*e*) Cool, add about 100 ml. of hot water, warm gently a minute or so to disintegrate the mass, transfer to a 250-ml. beaker, scrub the dish, and then remove stains by rubbing it with a few drops of hydrochloric acid.

(*f*) Carefully add 10 ml. of hydrochloric acid and 1 ml. of nitric acid, bring to a boil, and allow to boil awhile until the iron hydroxide is dissolved. Cool somewhat, add ammonia in excess, again bring to a boil, allow to settle a few minutes, filter through a common 9-cm. paper, wash five times by hot water, and discard the filtrate.

(*g*) By means of a wash-bottle jet, transfer the bulk of the precipitate from the paper into the beaker in which the precipitation was made, place the beaker beneath the funnel, and slowly pour around the paper a boiling mixture of 5 to 10 ml. of water and exactly 1 ml. of hydrochloric acid. As may be told by the color, this will dissolve the iron hydroxide, but may leave other constituents. However, do not be misled by a yellowish residue of titanium peroxide (TiO_3) which is sometimes formed. Remove the beaker and substitute a 180-ml. copper flask beneath the funnel to catch any drops from the funnel stem. It is not necessary to wash the paper.

(*h*) Bring the contents of the beaker to a boil, continue boiling a few minutes until the iron is dissolved completely, running the solution up the sides of the beaker, filter through the paper previously used into the copper flask, wash five times by hot water, discard the precipitate, boil the contents of the flask down to about 10 ml., run this liquid up on the sides of the flask to dissolve dried-out specks of iron chloride, cool, wash down the sides, add 1 ml. of potassium iodide solution, and titrate in an atmosphere of carbon dioxide by the standard thiosulfate solution, as described for the standardization by iron wire.

Deduct the number of milliliters used by a blank, multiply the Fe_2O_3 value in grams per milliliter by the number of milliliters used, and, since a 10-gram charge was used, move the decimal point one place to the right for per cent of Fe_2O_3.

Method for Sands Relatively High in Alumina

For sands containing several per cent of alumina, follow paragraphs *a*, *b*, and *c*, with the exception that the 10 ml. of sodium hydroxide solution recommended in (*c*), being insufficient, should be increased possibly to as much as 20 ml. to provide a liquid fusion. The addition of 1 ml. of sodium chlorate is omitted, there being no necessity for oxidizing carbonaceous matter and no wishing for converting ferrous iron to ferric, since a sodium sulfide separation is to be made. Continue as in paragraphs (*d*) and (*e*) and then pass to (*i*).

(*i*) To avoid subsequent tearing of the filter paper by the excessive causticity required to make a liquid fusion, neutralize a part of the alkalinity by a few milliliters of hydrochloric acid, and then to the still alkaline solution add 10 ml. of sodium sulfide solution. Bring to a boil and permit to stand until the supernatant liquor is yellowish, instead of greenish. Preferably, allow this precipitation to stand overnight because of the slowness with which it becomes complete.

(*j*) Filter, using a 9-cm. common paper, and wash several times by warm, sodium sulfide water. The filtrate should be yellow. Any greenish color should cause suspicion that some iron has passed into the filtrate. Discard the filtrate.

(*k*) By means of a fine jet, wash the bulk of the precipitate from the paper into the beaker in which the precipitation was made, and place it beneath the funnel. The black coloration left on the paper should be dissolved by a boiling mixture of 3 ml. of strong hydrochloric acid and 7 ml. of water poured around the edges and onto the dark spots of the paper. The iron sulfide will be dissolved even though at times there may be some black silver sulfide coloration left, which may be ignored. Wash the paper in hot water.

(*l*) Boil the solution until there is no odor of hydrogen sulfide, then add 1 ml. of nitric acid and evaporate to dryness to dehydrate silicic acid. Cool, add 5 ml. of water, 5 ml. of hydrochloric acid, and 1 ml. of nitric acid, bring to a boil, dilute to 100 ml., boil again, filter through a common 9-cm. paper, wash, breaking up the coagulated particles of silica, and discard the precipitate.

(*m*) Add an excess of ammonia to the filtrate, bring to a boil, allow to settle, and collect the ferric hydroxide on a common 9-cm. paper, washing by hot water. Discard the filtrate.

(*n*) Wash the precipitate from the paper into a copper flask and proceed as described before in preparation for titrating.

Comments

(*a*) The silver dishes may be 4 inches (10.16 cm.) wide and 2 inches (5.08 cm.) deep with rather flat bottoms. The metal may be about $^1/_{32}$ inch (0.079 cm.) thick. They weigh about 4 troy ounces (0.124 kg.) each. Platinum should not be used for the sodium hydroxide fusion. Pure silver is unacted upon by hydrofluoric acid and only slightly by dilute hydrochloric under the conditions prescribed, so the dishes will last some time. Ordinary or sterling silver, containing copper, should not be used, since any dissolved copper may precipitate in part with the iron hydroxide and raise the titration. The U. S. Government Mints at Philadelphia, Denver, and San Francisco, and the New York Assay Office produce electrolytic silver by the Moebius process, having a fineness of from 999.5 to 999.75 and containing no iron. Some manufacturing jewelers and silversmiths are able to secure such material from the mints and provide sheets for those who wish them. Manufacturers of electric fixtures may form these sheets into dishes. Unless the latter are familiar with the working of silver, they should be informed that silver should be annealed from time to time while being worked. This may be done by heating to low redness, say by a gasoline torch. These are relatively inexpensive. Chemical supply houses may be able to supply them, but the author has not found them stocked.

(*b*) Hydrofluoric acid, C. P. grade, is obtainable only in 1-pound (0.45-kg.) ceresin bottles. If a number of determinations are to be made, it is advisable to pour the contents of several into a large glass pitcher or some similar vessel which has been thoroughly dried and then coated with melted ceresin, the material of which the hydrofluoric acid bottle itself is made. Pour the melted wax into the vessel, carefully heat it, and allow the excess to run around the sides and drain out. The blended acid may be returned to the individual ceresin bottles. A blank from one is representative. There is no volatilization of iron in the absence of sulfuric acid, ordinarily used in a hydrofluoric acid rundown, as proved by evaporating "knowns."

(*c*) In order to account for the iron in fused caustic soda by running blanks, it is considered preferable to measure exact quantities of a solution rather than to attempt to weigh equal portions of this deliquescent substance. Were the pellets which are on the market of reasonably uniform weights, they would be highly desirable in avoiding the necessity for evaporating water, but they vary too much to enable one to count a certain number into each determination and blank.

Although the chlorate by itself would attack the silver pronouncedly, the sodium hydroxide present prevents this to some extent. Sodium chlorate melts at 248° C. and potassium chlorate at 368° C., so the sodic salt is preferable. Sodium hydroxide melts at 318° C. Sodium peroxide is undesirable as an oxidizer, since the reagent is too impure. It oxidizes silver and the combination produces a mess.

(*d*) The fusion with caustic soda and chlorate completely decomposes the hydrofluoric acid residue and eliminates organic matter, most of which is derived from the ceresin bottles. Should any organic matter remain, incomplete precipitation of the iron hydroxide would occur and permit of low results.

(*e*) Silver is somewhat soluble in strong hydrochloric acid, and therefore the rubbing with it should be done quickly.

(*f*) The residue in hydrochloric acid solution should be inspected for dark undecomposed particles, but all the sands tried have been thoroughly decomposed without the need of a pyrosulfate fusion.

If there is an odor of chlorine, it is probable that all organic matter has been destroyed.

The ammonium hydrate precipitate will contain ordinarily not only iron hydroxide, but silica and the hydroxides of aluminum, zirconium, and titanium, and possibly slight amounts of vanadium and copper. Should the latter two be present, they are not ordinarily in sufficient amounts to affect the thiosulfate titration.

(*g*) The "copper" flask is of glass, and its shape has been developed for ease of handling in making copper and other titrations in the West. After use, it may become coated inside by a white film. This may be removed by boiling a 50 per cent caustic soda solution in it and washing.

(*h*) The filtering of the dilute hydrochloric acid solution leaves much of the impurities, except aluminum, behind on the paper. The titration is not affected by what passes through.

(*i*) Although it is an annoying separation to make, sodium sulfide precipitation is used because no manipulation which has been noted or which was tried provides for a sufficiently complete precipitation of iron hydroxide by caustic soda. Further, the greater the excess, the more the iron found in the filtrate.

It has occurred to the author to add sufficient ferric chloride solution to the sodium hydroxide reagent to saturate it and provide a slight excess of ferric hydroxide, to allow the latter to settle, and to pipet clear supernatant liquor for fusions, for the purpose of doing away with the objectionable use of sodium sulfide and permitting filtering the sodium hydroxide solution almost immediately, but time to try it out and check it has not been available. The residue containing the iron hydroxide should be dissolved and run to dryness to dehydrate silicic acid, filtered, and the solution treated as described for precipitation by ammonia in paragraph (*m*) of Method.

(*j*) Slight amounts of vanadium seem to have the effect of carrying iron into the filtrate, thereby causing the green-colored solution. Long standing only will permit of complete precipitation and a yellowish filtrate.

A single sodium sulfide precipitation will not remove iron sulfide from aluminum, but does free it of enough to avoid the nuisance of having an excessive amount present in the iron hydroxide precipitate formed later (paragraph (*m*) of Method).

(*k*) The iron sulfide is readily dissolved. There should be no more than a film of sulfides left on the filter paper anyway, provided the precipitate has not been allowed to become dry before removal by the jet.

(*l*) When alumina is relatively high, it is difficult to remove all the silica by a hydrofluoric acid rundown, but the caustic soda fusion will take care of this. The gelatinous silicic acid formed by acidification is objectionable later on in the filtering of iron hydroxide and in the titrating by thiosulfate, so it is best to dehydrate it at this point and filter it off.

(*m*) No particular time of standing for complete precipitation by ammonia is necessary, provided the solution is brought to a boil.

(*n*) Were a sodium sulfide separation not made to free a small amount of iron from a relatively large quantity of aluminum, and were silica not removed, this titration would be prolonged so greatly, owing to entanglement, that uncertainty would be created as to when an end point is reached.

Literature Cited

(1) Bur. Standards, "Certificate Analyses, Standard Sample No. 81."
(2) Low, A. H., "Technical Methods of Ore Analysis," 9th ed., p. 80, Wiley, 1922.
(3) Lundell, G. E. F., and Knowles, H. B., Jr., *J. Am. Ceram. Soc.*, **11**, 119 (1928).
(4) Yoshida, I., *J. Chem. Soc. Japan*, **48**, 26 (1927).

Residual-Current Measurements in Control of Metal Solution in Milk[1,2]

H. T. Gebhardt[3] and H. H. Sommer

University of Wisconsin, Madison, Wis.

The solution of copper in milk occurs through the action of local elements in which the cathode consists of passive areas. The corrosion elements which are active in copper solution in milk may be studied by means of model elements, using copper anodes, and platinum or gold cathodes, or by using bright and oxidized copper electrodes. For copper, the current gives a qualitative measure of the solution rate under various conditions. From the current the amount of copper dissolving in milk may be calculated with fair approximation to the gravimetrically determined values.

The solution of nickel in all probability may be studied in a similar manner as copper. For other metals the current measurements give a qualitative indication of the probable solution rate, but the correct interpretation of the observed current requires more investigation.

The principle of the oxidimeter of Toedt, which was used mainly to measure the corrosion rate of iron and steel, may also be used successfully for measuring the solution rate of copper. Therefore, residual-current measurements may be used in the study of copper solution in practice.

THE problem of metal contamination in dairy products is important, as it involves not only the durability of dairy equipment, but also the flavor and keeping quality of the products. In recent years investigators have studied this problem, with the result that manufacturers of equipment have introduced new alloys designed to be more resistant to corrosion. The industry in general is in an expectant mood for more information on the problem.

The corrosiveness of many metals under various conditions has been investigated in laboratory corrosion tests, but useful data can be obtained only if in the laboratory experiment the corrosion factors are carefully controlled. Such tests require elaborate apparatus and consume appreciable time (*3*).

On the other hand, laboratory corrosion tests are often criticized (*3*, *9*) because the results of such tests are not directly applicable in practice. Corrosion conditions in practice are difficult to simulate in the laboratory. Various compromising methods have been suggested to meet the conditions of special practical problems. Unfortunately

[1] Received April 15, 1931. Presented before the Division of Agricultural and Food Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

[2] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station. The work was supported in part by a grant from the Special Research Fund of the University of Wisconsin.

[3] Present address, Control Laboratory, Nestlé's Milk Products, Inc., Marysville, Ohio.

most of these methods involve the use of special apparatus and require much time.

Among such methods, that of Toedt (*12–15*) appeared to be the simplest and most applicable for both laboratory and practical tests. Toedt devised an apparatus for measuring metal corrosion by residual-current measurements. He attempted to show that the current measurements give results which agree with the gravimetrically determined losses in weight of iron (*14*). These, however, were determined by a method which failed to provide for control of the velocity, and was open to other criticisms.

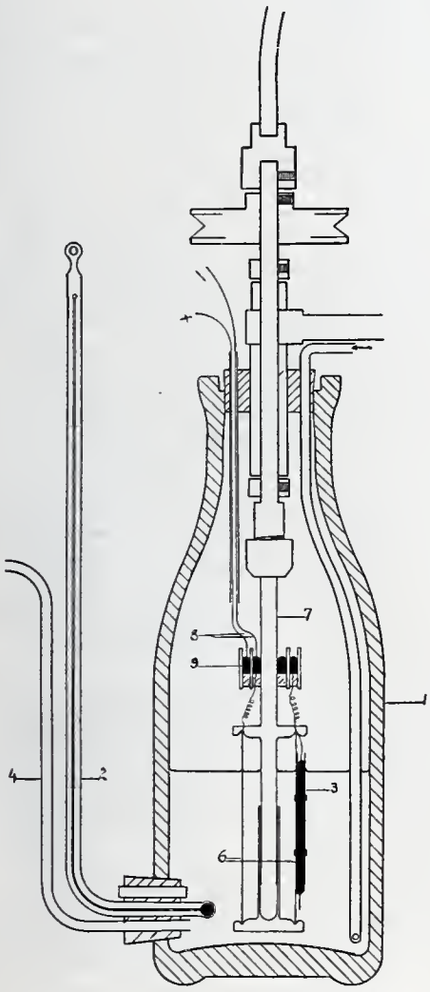


Figure 1—Sketch of Apparatus

This method of Toedt is based on the electrochemical theory (*10*) of metal solution, which assumes that the surface of the corroding metal consists of small local areas where the metal dissolves—the anode areas—and that the major part of the surface is passive and serves as the cathode in the corrosion element. The factors which cause the formation of corrosion elements have been studied by various investigators (*1, 2, 7, 8, 11*). Model elements which simulate the corrosion element can be prepared in the laboratory, and permit the study of the activity of the corrosion elements by measuring the (residual) current.[4] Since the apparatus devised by Toedt represents such a model element, this term will be used throughout this paper.

In the past year the solubility of metals in milk has been studied extensively in this laboratory (*4*). Abundant quantitative data on the corrosion rate of various metals were made available and appeared especially suited to serve as a basis for comparison with results furnished by residual-current measurements.

Most of the work up to the present time concerned the solution of copper in milk, but interesting observations were made also with other metals.

Method

The method for exposing the metal test pieces and the cathode metal (noble metal electrode) is illustrated in Figure 1. It is the same method as was used for gravimetric solubility tests (*4*). In Figure 1, number 1 indicates container for milk (quart bottle); 2, thermometer to control temperature of milk; 7, stirring device; 6, metal test piece; 3, platinum, gold, etc., electrodes; 4, potassium chloride–agar bridge to measure single potentials; 9, mercury commutator; and 8, "take-off" wires to galvanometer and potentiometer.

The arrangement of the apparatus for the current and e. m. f. measurements is shown in Figure 2, where *a*, *b*, indicates connection with the electrodes; *Sc*, *Sa*, switches; *A*, amperemeter; and *R*, resistance box. On the right side is shown the potentiometer.

The test metals were samples of commercial sheet metal. They were lightly scoured with Bon Ami powder before being immersed in the milk.

Solubility of Copper in Milk

Platinum, either plain or gold-plated, or gold electrodes were used as the cathodes in connection with copper. The preparation of the electrodes and the cleaning required special care (the best results were obtained with the method described by Livingston et al. (*6*), in slightly modified form).

General Observations—When the circuit was first closed, a very high current was observed, but it decreased rapidly during the first few minutes. After this, the current decrease continued for some time at a slow rate, which varied with individual electrodes.

Agitating the milk or the cathode caused the current to increase. Agitating the copper without agitating the milk in contact with the cathode had no effect on the magnitude of the current.

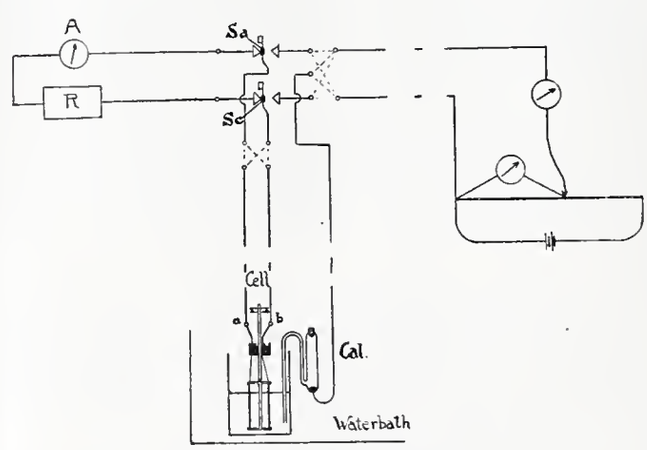


Figure 2—Arrangement of Apparatus for Current and E. m. f. Measurements

Effect of Acidity—The copper and the platinum electrodes (about 1.2 sq. cm. surface area), attached to the stirring device, were agitated in the milk at 23° C. Two such model elements were prepared. The current observations are given in Graph 1. After 23 minutes, 10 cc. of dilute lactic acid solution were added to the milk in one of the two samples. The current increased slightly after the first addition (the acid was added slowly), but soon the current decreased rapidly, and was smaller than in the control. After 27

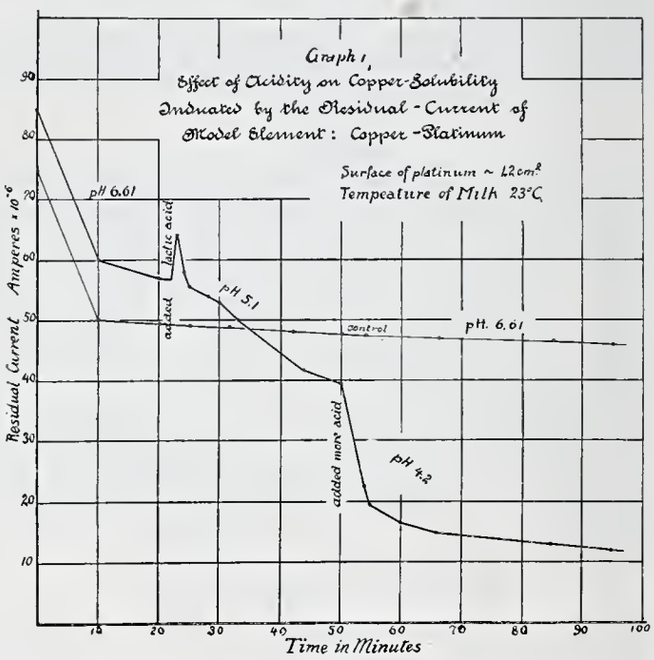
[4] The term "residual current" heretofore was applied to the current which, apparently independent of Ohms law, flows between two electrodes, when an external e. m. f. is applied which is below the decomposition potential (*5*).

The current of the local corrosion elements has not been named. Toedt proposed the term "oxygen-residual current" (Sauerstoff Reststrom) to be given to the current which is generated by model corrosion elements, such as platinum-iron, in an electrolyte solution. The current of similar elements in the literature occasionally is termed "depolarization current."

The present investigation on the nature of the current of model elements has revealed the fact that the current is identical in its physicochemical nature with the original residual current. For this reason it is termed briefly "residual current" in this paper.

minutes it was 39.5×10^{-6} as compared to 47.0×10^{-6} in the control, and the pH of the acid milk was 5.1 as compared to 6.61 for the control milk sample.

At this moment 10 cc. more acid was added. Immediately a similar drop of the current, as before, was produced. After the second addition of acid, the pH of the milk was 4.2.



The current decrease is in agreement with the results of gravimetric corrosion tests as previously reported (*4*), where it was found that the acid milk dissolved appreciably less copper than sweet milk, especially at higher temperatures.

The objection has been raised that possibly the decreased copper solution in milk acidified with lactic acid would be due to the reducing effect of lactic acid, and is not due to the increased hydrogen-ion concentration. To examine this objection, the above experiment was repeated using dilute sulfuric acid instead of the lactic acid.

The current as indicated in Graph 2 was observed. This shows that the effect of acid is the same whether lactic acid or sulfuric acid is used—i. e., the effect is due to the increased hydrogen-ion concentration.

Effect of Dissolved Oxygen—Copper solution in milk had previously (*4*) been found to increase appreciably when oxygen was bubbled through the milk during the exposure. On the other hand, when carbon dioxide was bubbled through the milk, copper solution decreased. This effect was attributed to the rinsing out of the dissolved oxygen from the milk.

Two experiments conducted to study the effect of dissolved oxygen on the current are reported in Graph 3. Curve *a′* illustrates the effect of increased oxygen concentration on the current; *a″*, the effect of rinsing out the dissolved oxygen with nitrogen (not purified commercial), and later of redissolving oxygen, on the current.

The current observed in these experiments and the solubility of copper as shown in the gravimetric tests are parallel when influenced by change of the oxygen content of the milk.

Curve *a′* decreased rapidly from its maximum about 12 minutes after the bubbling of oxygen through the milk had been started. This drop of the current was in all probability due to the beginning of passivity of the copper caused by the high oxygen concentration. This copper test piece showed a faint bluish interference color when removed from the milk, whereas the control test piece was untarnished, a phenomenon which had also been observed in previous gravimetric tests (*4*).

Effect of Temperature—The temperature of the water bath in these experiments increased gradually, and the temperature and current changes at certain times were noted, as shown in Graph 4. When the current was plotted against the temperature, curve *c* was obtained.

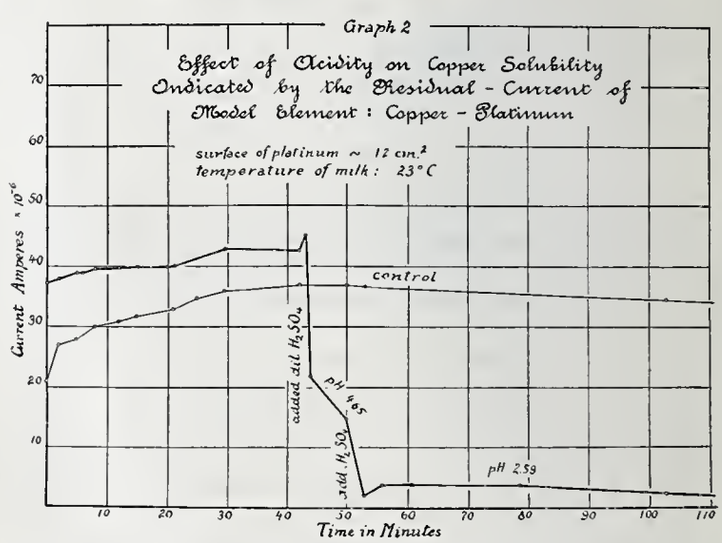
The amounts of copper dissolving were calculated (in terms of milligrams of copper dissolved, per square decimeter, per hour) from the cathode current density, as observed at certain temperatures. Comparison of the two curves, *a* for the gravimetrically determined values, and *b* for the calculated values, shows fair agreement of the two.

In previous work it had been found that the copper solubility increased at a logarithmic rate with the temperature up to 50° C. Similarly it was found that the current increases at a logarithmic rate up to 45° C., as shown in Graph 5. Above this temperature the observed current is less. The calculation of the dissolved copper from this experiment gives somewhat higher values than the gravimetrically determined values, as obtained after exposure for one hour. The calculated values are about as high as those obtained gravimetrically after exposure for one-half hour.

The calculation of the rate of copper solution is based on the assumption that equal amounts of hydrogen are plated out per unit of surface area (*12–14*) of the cathode in the model element, as on the cathodic surface areas of the copper. The total amount of hydrogen plated out is equivalent to the amount of copper which goes into solution, and for this reason one would be justified in calculating directly the amount of copper dissolving by applying Faraday's law:

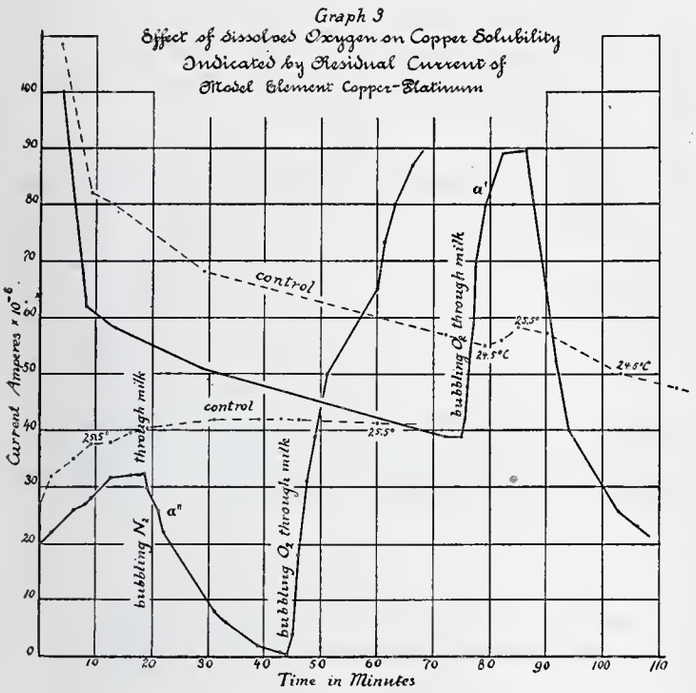
$$\text{mg./dm.}^2\text{/hr. Cu} = \frac{1.186 \text{ grams Cu} \times \text{current}}{\text{surface of cathode}}$$

Although the above-calculated values come quite close to the gravimetric values, the calculations involve some uncertainty because of the change of the current with time, whereas all the controllable factors remain constant (on the other hand, it is known that copper solution in milk de-



creases with time), but especially because the current is not strictly proportional to the measured surface area of the cathode metal. The cause of these discrepancies has been studied more in detail and will be discussed at another place.

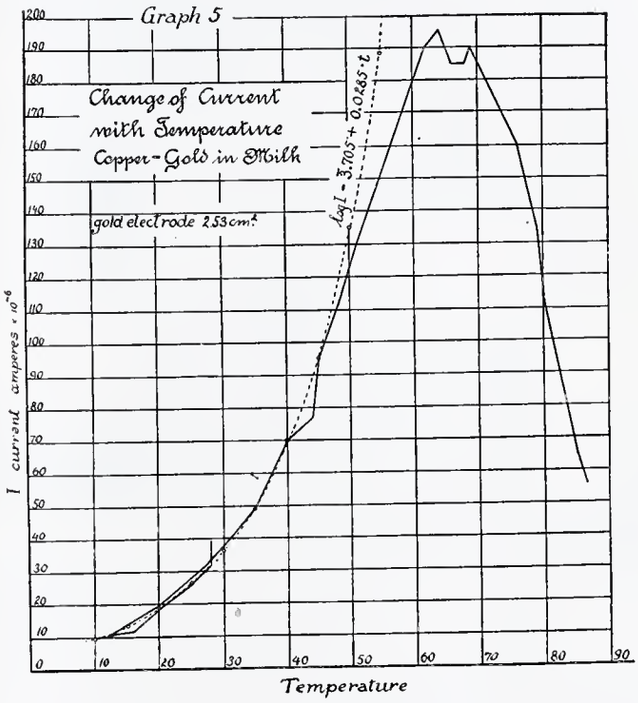
These observations with copper model elements evidently prove that the magnitude of the current is an indicator of the comparative rate of copper solution in milk under various conditions. However, they also present strong evidence that copper solution in milk takes place through the action



of local corrosion elements. The activity of these corrosion elements can be observed with fair accuracy on the model elements of copper combined with platinum or gold.

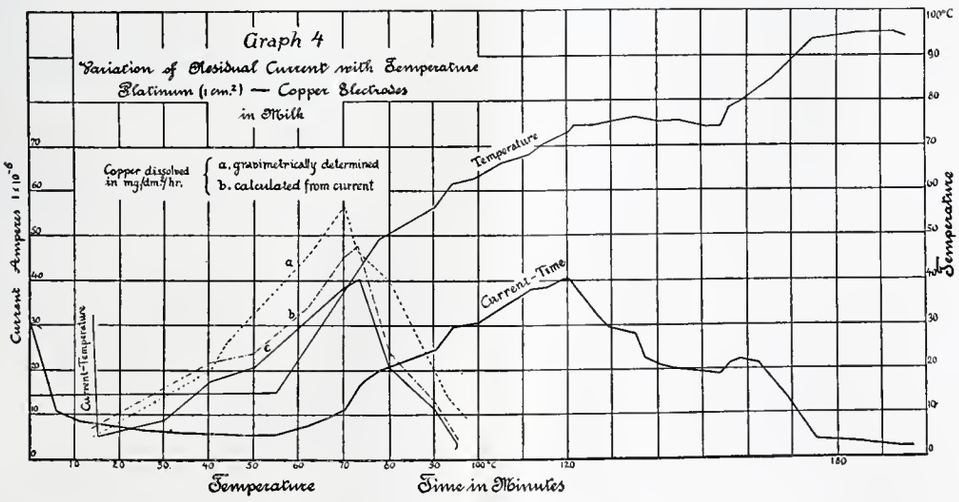
A Model Element of Copper Electrodes—The existence and the activity of corrosion elements, however, can be demonstrated in a more simple and striking manner. It was found that two copper test pieces, only one of which was freshly scoured with Bon Ami powder, when immersed in the milk and connected through a galvanometer, produced a strong current which was almost constant during an indefinite number of hours. This current had the same characteristics as the residual current of the model elements previously described. It is affected by agitation, dissolved oxygen, and temperature. But the current density on the cathodic test piece is less than on the noble metal electrodes. Obviously this is due to the fact that not the entire surface of the cathode test piece serves as cathode, and that in certain localities copper dissolves from it. The current density on the cathode areas, therefore, is greater than on the single test piece.

In Graph 6 the changes of the current with the temperature, as observed with one of the above model elements, is illustrated. The current is seen to increase at a logarithmic rate. The maximum current was obtained at 58° C., and above 65° C. it decreased rapidly, reached zero at 78° C., and immediately began to increase in the opposite direction. Apparently the high cathodic current density at 65° C. activated the previously cathodic surface areas on the copper and caused this test piece to become the anode in the model elements. No doubt this change of the roles of the anode and cathode metals is a periodic phenomenon. This mechanism evidently is of great practical importance



when copper serves as a heat-transmitting medium, as was indicated by a special experiment. This suggests that the rate of copper solution under such conditions must be very high.

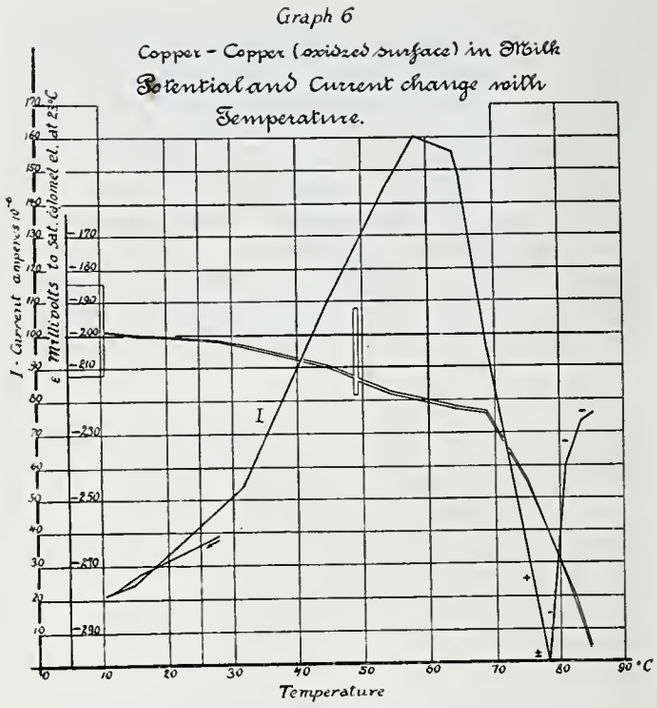
The activation of the copper due to high temperature (or high cathodic current density) is further indicated by



The difference between two copper test pieces consisted in a faint oxide film produced by exposure to air which produced passivity of the copper surface. This effect had been removed by scouring on the other copper blade.[5]

the drop of the single potentials of the copper at temperatures above 70° C.

[5] The change of the copper surface due to the exposure to air sometimes goes parallel with the production of a visible oxide film (which may be less soluble, or possibly non-conducting), but it appears that the passivity is not produced by this visible film, because the film could hardly explain why the single potential in milk is more positive. The production of a visible film (bluish) by immersion into dilute sodium sulfide solution renders the potential more positive, and the rate of solution, as indicated by the current, is greater from the coated metal than from the bright copper.



Solubility of Other Metals in Milk

The currents produced by various other metals in milk when connected with platinum or gold electrodes were studied. At the present time none of these have been sufficiently investigated to permit definite conclusions. A few general observations are here reported.

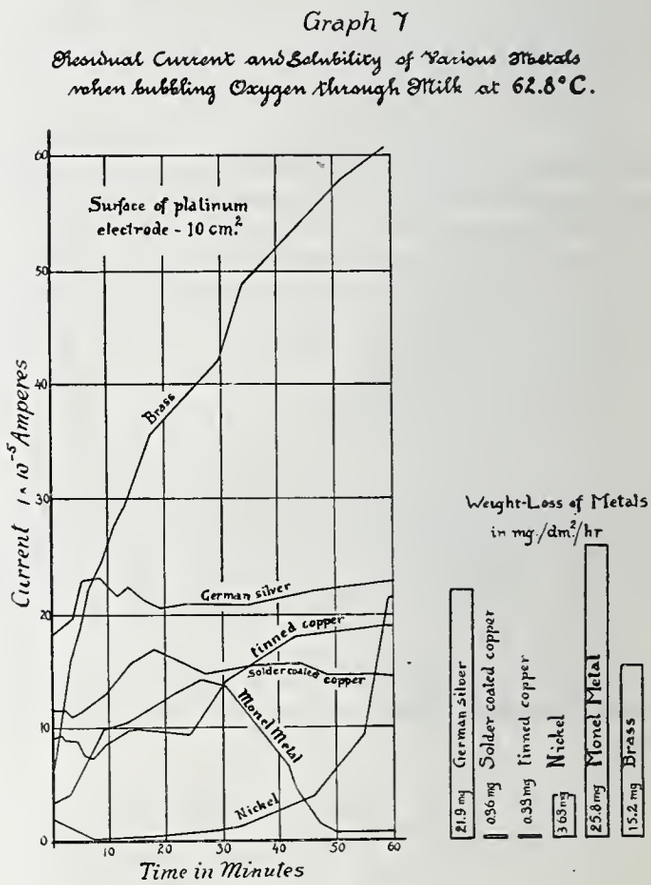
Nickel—The currents observed with nickel in milk under various conditions were very similar to those obtained with copper. In almost all cases higher currents were observed, the currents fluctuating more with time and the surface conditions of the nickel. These observations indicate the parallelism of the current and the actual weight losses, so that the current measurements may give information concerning the relative solution rate of nickel in the same manner as was possible for copper.

Aluminum, Zinc, and Tin—These metals differ as a group from the metals already mentioned and from the alloys in that they produce very high residual currents, although they actually dissolve but very little in milk. The current, therefore, is in no proportion to the amount of metal dissolving in the milk. At present no satisfactory explanation for this phenomenon can be given, but it appears that probably all the hydrogen, in amounts equivalent to the metal going into solution, is plated out at the noble metal surface. This was found to occur when zinc was dissolved in hydrochloric acid under hydrogen evolution when connected with a platinum electrode, as reported by Centnerszwer et al. (*1*). Further, the behavior of these metals in solution is largely changed when connected with more noble metals. Thus, aluminum, which otherwise is practically not dissolved by sweet milk, suffers appreciable pitting, and zinc dissolves more rapidly. Tin coatings apparently are not affected by the connection with platinum electrodes.

Various Alloys—Various alloys were studied in preliminary experiments. Obviously the interpretation of the current in this case is more difficult than with single metals, but from the results it appears that further study of residual currents will lead to a better understanding of the complicated corrosion mechanism of metal alloys. It is believed that residual-current measurements offer the best means for elucidating corrosion mechanisms.

In Graph 7 the current observations with various metals in combination with platinum in milk at 62.8° C., when oxygen was bubbled through the milk, are reported. For comparison with the gravimetrically determined weight losses, these are reported to the right.

The magnitude of the current and the corresponding weight losses are not in agreement. Nevertheless, the changes of the current during the experiments furnish valuable information concerning the corrosion rate and its variations with time. Thus the current indicates (1) for nickel, the disappearance of passivity (an oxide film); (2) for monel metal, the production of passivity; (3) for tinned copper and solder-coated copper, slight increase in the solution rate; (4) for German silver, only slight variations in the solution rate; (5) for brass, increased solution rate, and in all probability more rapid solution of copper, so that the relative surface of zinc increased, and thus zinc became the dominant metal determining the current.



Literature Cited

(1) Centnerszwer, W., and Straumanis, M., *Z. physik. Chem.*, **128**, 415, (1925).
(2) Evans, U. R., Ind. Eng. Chem., **17**, 383 (1925).
(3) Frazer, O. B. O., Ackerman, D. E., and Sands, J. W., *Ibid.*, **19**, 332 (1927).
(4) Gebhardt, H. T., and Sommer, H. H., "The Solubility of Metals in Milk," unpublished manuscript, to appear in *J. Dairy Sci.* (1931).
(5) Grube, G., "Grundzuege der theoretischen und angewandten Elektrochemie," Steinkopff, 1930.
(6) Livingston, J., Morgan, R., Lammert, O. M., and Campbell, Margaret A., *J. Am. Chem. Soc.*, **53**, 454 (1931).
(7) McKay, R. J., *Trans. Am. Electrochem. Soc.*, **41**, 201 (1922).
(8) McKay, R. J., Ind. Eng. Chem., **17**, 23 (1925).
(9) McKay, R. J., Am. Inst. of Mining and Met. Eng., *Tech. Pub.* **192**, Class E, Inst. Metals No. 73.
(10) Speller, F. N., Ind. Eng. Chem., **17**, 339 (1925).
(11) Thiel, A., and Eckell, J., *Z. Elektrochem.*, **33**, 370 (1927).
(12) Toedt, F., *Ibid.*, **34**, 587 (1928).
(13) Toedt, F., *Ibid.*, **34**, 591 (1928).
(14) Toedt, F., *Ibid.*, **34**, 853 (1928).
(15) Toedt, F., *Chem.-Ztg.*, **53**, 567 (1929).

AUTHOR INDEX

INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

VOLUME 3—1931

ADDLESTONE, J. A., AND FISH, F. H. Udit Coal Studies on Some Virginia Coals 155
AKERLOF, GOSTA, AND FOOTE, H. W. Low-Temperature Thermostat.. 389
ALBERTONI, G. J. New Autographic Machine for Testing Tensile Properties of Rubber 236
ALDRICH, E. W. Solubility of Water in Aviation Gasolines 348
ALESSANDRONI, H. V., CLIFFORD, G. E., WILKENS, G. A., HIXSON, A. W., AND WORK, L. T. Apparatus for Experimental Pyrolytic Production of Diphenyl 289
ALLDREDGE, S. M., AND SCOTT, W. W. Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium 32
ALLEN, W. F. Accurate and Adaptable Micro-Kjeldahl Method of Nitrogen Determination 239
ALSBERG, C. L., COOK, W. H., AND GRIFFING, E. P. Mill for Small Samples 102
AMBLER, J. A. Impurities in White Sugars. III—Determination of Labile Organic Sulfur 341
AND BYALL, S. Impurities in White Sugars. I—Determination of Phosphorus 136
Measurement of Color in Solutions of White Sugars 135
SNIDER, J. B., AND BYALL, S. Impurities in White Sugars. II—Determination of Sulfates, Sulfites, and Aldehyde-Sulfites 339
ANDREWS, J. R. Volumetric Barium Chromate Method for Sulfates... 361
ANDREWS, R., AND KESTER, E. B. Stillhead for Laboratory Columns. 373
ANSBACHER, STEFAN, REMINGTON, R. E., AND CULP, F. B. Copper Determination in Organic Matter 314

BAILAR, J. C., JR. Comparison of Solubilities of Calcium and Strontium *p*-Bromobenzoates in Acetone-Water Mixtures 362
BALCH, R. T. Measurement of Turbidity with a Spectrophotometer... 124
BEARD, L. C., JR., AND REIFF, O. M. Application of Oxalic Acid—Uranyl Acetate Actinometer to Measurement of Sunlight Intensity in Connection with Photochemical Changes in Gasoline 280
BENSON, H. K., AND HICKS, J. F. G., JR. Proposed Modification of Oxygen Consumed Method for Determination of Sea Water Pollution 30
BITTING, C. D., PICCARD, J., AND PETERSON, E. G. Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration. [*See* IND. ENG. CHEM., Anal. Ed., **2**, 294 (1930)] 225
BLACET, F. E., AND LEIGHTON, P. A. Dry Method of Microanalysis of Gases 266
BLANK, E. W. Device for Estimation of Density of Gems and Small Amounts of Solids 9
BLATCHLEY, W. H. Elimination of Sulfur in Carbon Determinations by Direct Combustion 13
BOLLEN, W. B. Improved Hydrogen-Electrode Cell for Determination of pH 203
BONNAR, R. U., AND THOMPSON, T. G. Buffer Capacity of Sea Water.. 393
BONNER, W. D., AND ROMEYN, HENDRICK, JR. Oxidation of Ferrous Iron by Iodine in Presence of Phosphate and Non-Existence of Ferriphosphate Complex 85
BOYD, J. H., JR., AND OBERSEIDER, J. L. Effect of Light on Determination of Ethylene 123
BRADLEY, T. F. Methods for Detection and Identification of Synthetic Resins 304
BROPHY, D. H. Electrolytic Determination of Cobalt 363
BROWN, D. J., MOSS, J. A., AND WILLIAMS, J. B. Determination of Lead as Chromate in Presence of Perchloric Acid 134
BUSH, M. T., AND SCHWARTZ, A. M. Flow Divider for Fractionation under Diminished Pressure 138
BUSWELL, A. M., AND PEARSON, E. L. Sludge Ripeness Studies 359
BYALL, S., AND AMBLER, J. A. Impurities in White Sugars. I—Determination of Phosphorus 136
Measurement of Color in Solutions of White Sugars 135
AMBLER, J. A., AND SNIDER, J. B. Impurities in White Sugars. II—Determination of Sulfates, Sulfites, and Aldehyde-Sulfites 339

CARTER, R. H. Determination of Barium Fluosilicate Spray Residue 146
CASSAR, H. A. Simple Laboratory Autoclave 197
CHAPMAN, H. D. Notes on Use of Glass Color Standards for Determination of Phosphorus by Deniges Colorimetric Method 282
CHU, T. L., AND HAN, J. E. S. Benzidine Method for Determination of Acetic Acid in Lead Acetate 379
CLARKE, B. L., WOOTEN, L. A., AND COMPTON, K. G. Potentiometric Titration in Non-Aqueous Solutions. I—Differential Method for Determining Oil Acidity 321
CLARKE, LOYAL, AND DAVINSON, J. M. Rapid Volumetric Method for Determination of Potassium 324
CLIFFORD, G. E., WILKENS, G. A., HIXSON, A. W., WORK, L. T., AND ALESSANDRONI, H. V. Apparatus for Experimental Pyrolytic Production of Diphenyl 289
COLLINS, G. W. Irregularities in Sodium Determination by Sodium Sulfate Method 291
COLLINS, W. D., et al. Recommended Specifications for Analytical Reagent Chemicals 221
COMPTON, K. G., CLARKE, B. L., AND WOOTEN, L. A. Potentiometric Titration in Non-Aqueous Solutions. I—Differential Method for Determining Oil Acidity 321
COOK, W. H., GRIFFING, E. P., AND ALSBERG, C. L. Mill for Small Samples 102
COONS, C. C. Continuous Measurement of pH with Quinhydrone Electrodes 402
CORNWELL, R. T. K. Micro-Absorption Tube with Mercury Seals.... 4
CRAIG, RODERICK, AND KIRK, P. L. Improved Technic for Microgravimetric Analysis 345
CRANDALL, G. S., DAVIS, H. S., AND HIGBEE, W. E., JR. Problems in Estimation of Unsaturated Hydrocarbons in Gases. III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture 108
CULP, F. B., ANSBACHER, STEFAN, AND REMINGTON, R. E. Copper Determination in Organic Matter 314
CUNNINGHAM, T. R. Determination of Aluminum in Ferrochromium and Chromium Metal 103
AND HAMNER, H. L. Rapid Colorimetric Method for Determination of Molybdenum in Plain Carbon and Alloy Steels 106
AND PRICE, R. J. Determination of Zirconium in Plain Carbon and Alloy Steels 105

DANIELS, A. S. Dish for Toxicity Tests 358
DAVENPORT, J. E., AND EVANS, R. N. Potentiometric Determination of Acidity in Insulating Oils 82
DAVINSON, J. M., AND CLARKE, LOYAL. Rapid Volumetric Method for Determination of Potassium 324
DAVIES, J. M., AND DIETERICH, E. O. Scorching, and Other Plasticity Changes in Rubber Compounds on Heating 297
DAVIS, H. S., CRANDALL, G. S., AND HIGBEE, W. E., JR. Problems in Estimation of Unsaturated Hydrocarbons in Gases. III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture 108
DAVIS, J. D. Plastometer. New Instrument for Measuring Plastic Properties of Coal 43
DAVIS, R. O. E., AND SCHOLL, W. Method for Analysis of Volatile Compounds Containing Carbon, Hydrogen, and Nitrogen 276
DEGROOTE, MELVIN, KEISER, BERNHARD, WIRTEL, A. F., AND MONSON L. T. Analysis of Fatty Modifications Obtained by Action of Sulfuric Acid 243
DELANO, P. H., AND SCHRENK, W. T. Electrolytic Determination of Lead as Lead Dioxide 27
DEMAREST, J. V., AND RIEMAN, WM., 3RD. Potentiometric Determination of Saponification Number of Mixtures of Asphalt and Drying Oils 15
DIETERICH, E. O., AND DAVIES, J. M. Scorching, and Other Plasticity Changes in Rubber Compounds on Heating 297
AND HAHN, S. H. Graphical Tensile-Testing Machine for Rubber Threads 218
DOUGHERTY, G. T. Indirect Estimation of Silicon in 48 to 52 Per Cent Ferrosilicons 158
DYKINS, F. A., AND ENGLIS, D. T. Determination of Glucose in Presence of Fructose and Glycine by Iodometric Method 21
Effect of Amino Acids upon Rotation of Glucose and Fructose and Its Significance to Determination of Sucrose by Double Polarization Methods 17

EDWARDS, G. P., AND MOHLMAN, F. W. Determination of Carbon in Sewage and Industrial Wastes 119
ENGLIS, D. T., AND DYKINS, F. A. Determination of Glucose in Presence of Fructose and Glycine by Iodometric Method 21
Effect of Amino Acids upon Rotation of Glucose and Fructose and Its Significance to Determination of Sucrose by Double Polarization Methods 17
ERNST, R. C., PRAGOFF, E., JR., AND LITKENHOUS, E. E. Hydrogen-Ion Concentration and Color of Lead Chromate Pigments 174
EVANS, R. N., AND DAVENPORT, J. E. Potentiometric Determination of Acidity in Insulating Oils 82
EVENSON, O. L., AND NAGEL, R. H. Quantitative Estimation of Amaranth and Tartrazine in Food Color Mixture 260
Use of Buffers in Determination of Color by Means of Titanium Trichloride—II 167

FAIRBROTHER, A. M., AND WISE, L. E. Chemistry of Wood—III. Part 1—Comparison of Two Methods for Determination of Lignin 253
FERGUSON, G. E., OLSEN, J. C., SABETTA, V. J., AND SCHEFLAN, LEOPOLD. Quantitative Determination of Phosgene 189
FISH, F. H., AND ADDLESTONE, J. A. Unit Coal Studies on Some Virginia Coals 155
FOOTE, H. W., AND AKERLOF, GOSTA. Low-Temperature Thermostat. 389
FOOTE, M. E., AND NICHOLS, M. S. Distillation of Free Ammonia Nitrogen from Buffered Solutions 311
FORSEE, W. T., AND PIERCE, J. S. Detection of Cadmium 188
FRANCIS, A. G., AND PARSONS, A. T. Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration. [*See* IND. ENG. CHEM., Anal. Ed., **2**, 294 (1930)] 225
FUDGE, J. F. Apparatus for Continuous Leaching with Suction 114
FULMER, E. I. Quantitative Separation of Copper and Cadmium by Reduction of Their Salts with Potassium Formate 257
FULTON, C. C. Hehner Test for Formaldehyde 199
Opium Alkaloids as Reagents for Formaldehyde 200
FURMAN, N. H. Electroanalytical Separations in Ammoniacal Fluoride Solutions. I—Separation of Copper from Arsenic and Antimony 217

GEBHARDT, H. T., AND SOMMER, H. H. Determination of Copper in Dairy Products 24

Residual-Current Measurements in Control of Metal Solution in Milk 414
GEHMAN, S. D., AND WARD, J. S. Microturbidimeter for Determination of Rubber Content of Latex 300
GIBSON, R. C., AND WILLARD, H. H. Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid (Correction, 226) 88
GOEHLER, O. E., AND SMITH, G. F. Dissociation of Concentrated Perchloric Acid during Vacuum Distillation at Moderately Low Pressures 55
Oxonium Perchlorate as Reference Standard for Construction of Specific Gravity–Percentage Composition Table for Strong Perchloric Acid Solutions 61
Oxonium Structure of Hydrated Perchloric Acid 58
Purification of Perchloric Acid by Vacuum Distillation 48
GRAY, H. LEB., MURRAY, T. F., JR., AND STAUD, C. J. Acid Value of Cellulose Fatty Acid Esters and Rapid Analysis of Certain Cellulose Acetates 269
GREEN, JESSE. Use of Steam for Kjeldahl Distillation of Nitrogen 160
GRETTIE, D. P., AND NEWTON, R. C. Measurement of Rate of Formation of Oxidative Decomposition Products in Fats and Oils 171
GRIFFING, E. P., COOK, W. H., AND ALSBERG, C. L. Mill for Small Samples 102
GUSTAFSON, H., AND KEAN, R. H. Some Factors Influencing Soap Tests for Hardness 355

HAHN, S. H., AND DIETERICH, E. O. Graphical Tensile-Testing Machine for Rubber Threads 218
HAMNER, H. L., AND CUNNINGHAM, T. R. Rapid Colorimetric Method for Determination of Molybdenum in Plain Carbon and Alloy Steels 106
HAN, J. E. S., AND CHU, T. L. Benzidine Method for Determination of Acetic Acid in Lead Acetate 379
HARADA, TAICHI. Estimation of Diastatic Enzyme Preparations. Taka-Diastase, Malt Diastase, and Pancreatic Diastase 1
HARING, M. M., WITH WORTHINGTON, K. K. Methods for Determining Solubilities of Some Fluosilicates 7
HARLOW, W. M., AND WISE, L. E. Chemistry of Wood—III. Part 2—Comparison of Two Methods for Preparation of Lignin from Wood 254
HATFIELD, W. D., AND MORKERT, K. H. Easy Method of Marking Chemical Glassware 242
HICKS, J. F. G., JR., AND BENSON, H. K. Proposed Modification of Oxygen Consumed Method for Determination of Sea Water Pollution 30
HIGBEE, W. E., JR., DAVIS, H. S., AND CRANDALL, G. S. Problems in Estimation of Unsaturated Hydrocarbons in Gases. III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture 108
HIXSON, A. W., WORK, L. T., ALESSANDRONI, H. V., CLIFFORD, G. E., AND WILKENS, G. A. Apparatus for Experimental Pyrolytic Production of Diphenyl 289
HOLMES, C. R., AND KESTER, E. B. Analysis of Light Oils from Low- and Intermediate-Temperature Carbonization 292
HOLMES, R. L., AND LOTHROP, R. E. Determination of Dextrose and Levulose in Honey by Use of Iodine-Oxidation Method 334
HOPKINS, H. C., PARR, S. W., AND MITCHELL, D. R. Fusain 64
HOUGHTON, W. F., AND ROBB, J. A. Alignment Chart for Estimating Viscosity-Gravity Constant of Petroleum Lubricating Oils 144
HOWES, C. C., AND JACOBS, C. B. Should a Change Be Made in Analytical Procedure for Evaluating Available Phosphoric Acid Content of Fertilizer Materials? 70

ISAACS, AARON, WICHERS, EDWARD, AND SCHOONOVER, I. C. Two Hundred Reagent Chemicals—Good and Bad 227

JACOB, K. D., AND REYNOLDS, D. S. Effect of Certain Forms of Silica on Determination of Fluorine by Volatilization Method 371
Method for Determination of Fluorine in Phosphate Rock and Phosphatic Slags 366
JACOBS, C. B., AND HOWES, C. C. Should a Change Be Made in Analytical Procedure for Evaluating Available Phosphoric Acid Content of Fertilizer Materials? 70
JACOBS, M. B., AND JAFFE, LEON. Method for Identification of Common Gums 210
JAFFE, LEON, AND JACOBS, M. B. Method for Identification of Common Gums 210
JAMES, L. H. Modified Ford-Williams Method 31
Volumetric Determination of Chromium and Nickel in Same Solution 258
JONES, R. L. New Substrates for Use in Detecting Proteolytic Activity 149

KAMEDA, TOHRU, AND KOLTHOFF, I. M. Conductometric Titration of Sulfate and Barium 129
KARRER, E. Modified Balance for Approximate and Quick Weighing 112
KEAN, R. H., AND GUSTAFSON, H. Some Factors Influencing Soap Tests for Hardness 355
KEARSLEY, E. P. W., AND ROBERTS, G. L. Measurement of Effect of Carbon Black on Fluidity of Printing Ink 310
KEISER, BERNHARD, WIRTEL, A. F., MONSON, L. T., AND DEGROOTE, MELVIN. Analysis of Fatty Modifications Obtained by Action of Sulfuric Acid 243
KERN, E. W., AND SCHUH, A. E. Measurement of Abrasion Resistance. I—Paints, Varnishes, and Lacquers 72
KESTER, E. B., AND ANDREWS, R. Stillhead for Laboratory Columns. 373
AND HOLMES, C. R. Analysis of Light Oils from Low- and Intermediate-Temperature Carbonization 292
AND POHLE, W. D. Determination of Olefin, Aromatic, and Paraffin Hydrocarbons in Neutral Oil from Coal Tar 294
KILLEFFER, D. H. Solid Carbon Dioxide in Laboratory Technic 386
KING, E. J. Colorimetric Determination of Silica. [*See* IND. ENG. CHEM., Anal. Ed., 2, 276 (1930)] 117
KING, R. H. A Degree Brix–Total Solid Relationship. Study of Possible Theoretical Brix Correction Factor for Approximation of Solids by Drying Using Carbonate Ash Determination 230
KIRK, P. L., AND CRAIG, RODERICK. Improved Technic for Microgravimetric Analysis 345
KITSUTA, K., AND SALTER, R. M. Availability of Phosphoric Acid in Ammoniated Superphosphates. Proposed Method for Estimation 331
KOBE, K. A. Analysis of Three Hydrocarbons by Combustion 262
Modified Slow-Combustion Pipet 159
KOCH, W. W., AND SMITH, G. F. Perchloric Acid as New Standard in Acidimetry 52
KOLTHOFF, I. M., AND KAMEDA, TOHRU. Conductometric Titration of Sulfate and Barium 129
AND PEARSON, E. A. Stability of Potassium Ferrocyanide Solutions 381
AND SANDELL, E. B. Direct and Reverse Titration of Sulfuric Acid with Barium Hydroxide 115

LAURO, M. F. Use of Selerium as Catalyst in Determination of Nitrogen by Kjeldahl Method 401
LEIGHTON, P. A., AND BLACET, F. E. Dry Method of Microanalysis of Gases 266
LITKENHOUS, E. E., ERNST, R. C., AND PRAGOFF, E., JR. Hydrogen-Ion Concentration and Color of Lead Chromate Pigments 174
LOCKHART, L. B. Ignition Losses in Potash Analyses of Triple Superphosphate Mixtures 407
LOTHROP, R. E., AND HOLMES, R. L. Determination of Dextrose and Levulose in Honey by Use of Iodine-Oxidation Method 334
LOUGH, S. A. Large-Scale Soxhlet Extractor 344

MALHOTRA, R. C. Notes on Determination of Hemicelluloses 161
MARTI, W. C., AND MARTINEK, M. J. Practical Methods of Detecting and Estimating Methyl Chloride in Air and Foods 408
MARTINEK, M. J., AND MARTI, W. C. Practical Methods of Detecting and Estimating Methyl Chloride in Air and Foods 408
MCCOY, J. M. Determination of Smoking Point of Fats 347
MCCRUMB, F. R. Use of Wide-Range Indicators for Determination of pH 233
MCGAVACK, J., AND RUMBOLD, J. S. Determination of pH of Ammonia Latex 94
MCKINNEY, D. S. Interpretation of Water Analysis 192
MEHRING, A. L. Measurement of Drillability of Fertilizers 34
MILLER, G. W., AND PALMER, H. F. Determination of Alkalinity of Reclaimed Rubber 45
MITCHELL, D. R., PARR, S. W., AND HOPKINS, H. C. Fusain 64
MOHLMAN, F. W., AND EDWARDS, G. P. Determination of Carbon in Sewage and Industrial Wastes 119
MONSON, L. T., DEGROOTE, MELVIN, KEISER, BERNHARD, AND WIRTELL, A. F. Analysis of Fatty Modifications Obtained by Action of Sulfuric Acid 243
MORKERT, K. H., AND HATFIELD, W. D. Easy Method of Marking Chemical Glassware 242
MORRIS, H. P., NELSON, J. W., AND PALMER, L. S. Quantitative Determination of Calcium, Magnesium, and Phosphorus in Feedstuffs and Cattle Excreta 164
MOSS, J. A., WILLIAMS, J. B., AND BROWN, D. J. Determination of Lead as Chromate in Presence of Perchloric Acid 134
MÜLLER, R. H., AND PARTRIDGE, H. M. Determination of Hydrogen-Ion Concentration with Photoelectric Colorimeter 169
MURRAY, T. F., JR., STAUD, C. J., AND GRAY, H. LEB. Acid Value of Cellulose Fatty Acid Esters and Rapid Analysis of Certain Cellulose Acetates 269

NAGEL, R. H., AND EVENSON, O. L. Quantitative Estimation of Amaranth and Tartrazine in Food Color Mixture 260
Use of Buffers in Determination of Color by Means of Titanium Trichloride—II 167
NELSON, J. W., MORRIS, H. P., AND PALMER, L. S. Quantitative Determination of Calcium, Magnesium, and Phosphorus in Feedstuffs and Cattle Excreta 164
NEWTON, R. C., AND GRETTIE, D. P. Measurement of Rate of Formation of Oxidative Decomposition Products in Fats and Oils. 171
NICHOLS, M. L. Anodic Precipitation of Lead Peroxide 384
NICHOLS, M. S., AND FOOTE, M. E. Distillation of Free Ammonia Nitrogen from Buffered Solutions 311
NIEDERL, J. B., AND TRAUTZ, O. R. Absolute Determination of Nitrogen in Organic Compounds 151
NIEUWLAND, J. A., AND VAUGHN, T. H. Determination of Organic Halogen by Liquid Ammonia-Sodium Process 274
NISSEN, B. H. The pH of Butter and Its Relation to Titratable Acidity 374

OBERSEIDER, J. L., AND BOYD, J. H., JR. Effect of Light on Determination of Ethylene 123
O'LEARY, W. J., AND PAPISH, JACOB. Arc Spectrographic Estimation of Chromium in Ruby 11
OLSEN, J. C., FERGUSON, G. E., SABETTA, V. J., AND SCHEFLAN, LEOPOLD. Quantitative Determination of Phosgene 189
OSBURN, O. L., AND WERKMAN, C. H. Determination of Butyl and Ethyl Alcohols in Mixtures 387
Determination of Organic Acids. V—Application of Partition Method to Quantitative Determination of Acetic, Propionic, and Butyric Acids in Mixture 264
OTHMER, D. F. Glass Temperature and Float Regulators 139

PALKIN, S. Improved Gauze-Plate Laboratory Rectifying Column. 377
PALMER, H. F., AND MILLER, G. W. Determination of Alkalinity of Reclaimed Rubber 45
PALMER, L. S., MORRIS, H. P., AND NELSON, J. W. Quantitative Determination of Calcium, Magnesium, and Phosphorus in Feedstuffs and Cattle Excreta 164
PAPISH, JACOB, AND O'LEARY, W. J. Arc Spectrographic Estimation of Chromium in Ruby 11
PARK, BARTHOLOW. Iodide Method for Copper 77
PARR, S. W., HOPKINS, H. C., AND MITCHELL, D. R. Fusain 64
AND STALEY, W. D. Determination of Sulfur by Means of Turbidimeter 66
Studies in Adiabatic Calorimetry 396
PARSONS, A. T., AND FRANCIS, A. G. Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration. [*See* IND. ENG. CHEM., Anal. Ed., 2, 294 (1930)] 225
PARTRIDGE, H. M., AND MÜLLER, R. H. Determination of Hydrogen-Ion Concentration with Photoelectric Colorimeter 169
PEARSON, E. A., AND KOLTHOFF, I. M. Stability of Potassium Ferrocyanide Solutions 381
PEARSON, E. L., AND BUSWELL, A. M. Sludge Ripeness Studies 359
PETERSON, E. G., BITTING, C. D., AND PICCARD, J. Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration. [*See* IND. ENG. CHEM., Anal. Ed., 2, 294 (1930)] 225

PETTYJOHN, E. S. Portable Equipment for Crushing and Quartering Samples of Coal, Coke, and Other Lumpy Materials 163
PICCARD, J., PETERSON, E. G., AND BITTING, C. D. Determination of Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration. [*See* IND. ENG. CHEM., Anal. Ed., **2**, 294 (1930)] 225
PIERCE, J. S., AND FORSEE, W. T. Detection of Cadmium 188
PONBIELNIAK, W. J. Apparatus and Methods for Precise Fractional-Distillation Analysis 177
POHLE, W. D., AND KESTER, E. B. Determination of Olefin, Aromatic, and Paraffin Hydrocarbons in Neutral Oil from Coal Tar 294
POTH, E. J. Generator for Production of Carbon Dioxide of High Purity 202
PRAGOFF, E., JR., ERNST, R. C., AND LITKENHOUS, E. E. Hydrogen-Ion Concentration and Color of Lead Chromate Pigments 174
PRAMME, M. H. Determination of Glycerol in Greases 232
PRICE, R. J., AND CUNNINGHAM, T. R. Determination of Zirconium in Plain Carbon and Alloy Steels 105

RAKESTRAW, D. R., AND RHODES, F. H. Comparative Efficiencies of Gas-Washing Bottles 143
RASK, O. S., AND TOURTELLOTTE, DEE. Spectrographic Determination of Aluminum in Biological Ashes 97
REIFF, O. M., AND BEARD, L. C., JR. Application of Oxalic Acid–Uranyl Acetate Actinometer to Measurement of Sunlight Intensity in Connection with Photochemical Changes in Gasoline 280
REMINGTON, R. E., CULP, F. B., AND ANSBACHER, STEFAN. Copper Determination in Organic Matter 314
REYNOLDS, D. S., AND JACOB, K. D. Effect of Certain Forms of Silica on Determination of Fluorine by Volatilization Method 371
Method for Determination of Fluorine in Phosphate Rock and Phosphatic Slags 366
RHODES, F. H., AND RAKESTRAW, D. R. Comparative Efficiencies of Gas-Washing Bottles 143
RIEMAN, WM., 3RD, AND DEMAREST, J. V. Potentiometric Determination of Saponification Number of Mixtures of Asphalt and Drying Oils 15
RIPPERTON, J. C. Measurement of Consistency of Starch Solutions 152
ROBB, J. A., AND HOUGHTON, W. F. Alignment Chart for Estimating Viscosity-Gravity Constant of Petroleum Lubricating Oils 144
ROBERTS, G. L., AND KEARSLEY, E. P. W. Measurement of Effect of Carbon Black on Fluidity of Printing Ink 310
ROBERTSON, A. C. Simple and Easily Constructed Gas-Pressure Regulator 383
ROBERTSON, A. E., AND ROSEN, R. Analysis of Gaseous Hydrocarbons. A Short-Cut Method 284
ROBERTSON, G. R. Hydrogen-Ion Determinations with Low-Resistance Glass Electrodes 5
ROLLER, P. S. Accurate Air Separator for Fine Powders 212
ROMEYN, HENDRICK, JR., AND BONNER, W. D. Oxidation of Ferrous Iron by Iodine in Presence of Phosphate and Non-Existence of Ferriphosphate Complex 85
ROSEN, R., AND ROBERTSON, A. E. Analysis of Gaseous Hydrocarbons. A Short-Cut Method 284
ROWE, L. F., AND SKAU, E. L. Further Applications of the Centrifugal Filtration Tube 147
RUMBOLD, J. S., AND MCGAVACK, J. Determination of pH of Ammonia Latex 94
RUMMEL, J. K. Estimation of Solids in Steam by Conductivity 317
RYSSELBERGE, P. J., VAN. Quantitative Determination of Potassium by Sodium Cobaltinitrite Method 3

SABETTA, V. J., SCHEFLAN, LEOPOLD, FERGUSON, G. E., AND OLSEN, J. C. Quantitative Determination of Phosgene 189
SALTER, R. M., AND KITSUTA, K. Availability of Phosphoric Acid in Ammoniated Superphosphates. Proposed Method for Estimation 331
SANDELL, E. B., AND KOLTHOFF, I. M. Direct and Reverse Titration of Sulfuric Acid with Barium Hydroxide 115
SANDERS, M. T. Study of Official Method of Bleaching Test of American Oil Chemists' Society. [*See* IND. ENG. CHEM., Anal. Ed., **2**, 374 (1930)] 226
SANDIN, R. B., AND STOVER, N. M. Use of Boric Acid in Micro-Kjeldahl Determination of Nitrogen 240
SANDO, C. E. Electrically-Heated Melting Point Apparatus 65
SASCHEK, W. J. Microanalysis with an Ordinary Balance. I—Determination of Nitrogen by Micro-Dumas Method 198
SATTLER, LOUIS, AND ZERBAN, F. W. Ash and Electrical Conductivity of Refined Cane Sugars 41
Conductometric Formula for Determining Ash in Both Raw and Refinery Sirups and Molasses 38
Studies on Turbidity in Sugar Products. I—Relation between Intensity of Tyndall Beam and Depth and Concentration of Solution 326
SCARRITT, E. W. Determination of Phosphates in Presence of Silica in Boiler Water 23
SCHARNAGEL, A. R., AND TRUSTY, A. W. Determination of Hydrogen Sulfide in Refinery Still Gases 29
SCHEFLAN, LEOPOLD, OLSEN, J. C., FERGUSON, G. E., AND SABETTA, V. J. Quantitative Determination of Phosgene 189
SCHOLL, W., AND DAVIS, R. O. E. Method for Analysis of Volatile Compounds Containing Carbon, Hydrogen, and Nitrogen 276
SCHOONOVER, I. C., WICHERS, EDWARD, AND ISAACS, AARON. Two Hundred Reagent Chemicals—Good and Bad 227
SCHRENK, W. T., AND DELANO, P. H. Electrolytic Determination of Lead as Lead Dioxide 27
SCHUH, A. E., AND KERN, E. W. Measurement of Abrasion Resistance. I—Paints, Varnishes, and Lacquers 72
SCHWARTZ, A. M., AND BUSH, M. T. Flow Divider for Fractionation under Diminished Pressure 138
SCOTT, R. D. Application of Bromine Method in Determination of Phenol and Cresols 67
SCOTT, W. W., AND ALLDREDGE, S. M. Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium 32
SCRIBNER, A. K. Moisture Content of Liquid Sulfur Dioxide 255
SHAW, J. A. Determination of Phenols in Water Solution. Adaptation of Bromine Method to Include Range of 1 to 75 p. p. m. 273
SHELBERG, E. F., AND TABERN, D. L. Determination of Sodium in Organic Compounds. Use of Uranyl Acetate Method 278
SHREWSBURY, C. L. Extractor for Biological Products 320
SKAU, E. L., AND ROWE, L. F. Further Applications of the Centrifugal Filtration Tube 147
SKINNER, L. B. Thiosulfate Titrations of Small Amounts of Iron in Glass Sands 411
SMITH, G. F., AND GOEHLER, O. E. Dissociation of Concentrated Perchloric Acid during Vacuum Distillation at Moderately Low Pressures 55
Oxonium Perchlorate as Reference Standard for Construction of Specific Gravity–Percentage Composition Table for Strong Perchloric Acid Solutions 61
Oxonium Structure of Hydrated Perchloric Acid 58
Purification of Perchloric Acid by Vacuum Distillation 48
AND KOCH, W. W. Perchloric Acid as New Standard in Acidimetry 52
SMITH, W. C. Determination of Small Quantities of Sulfur and Chlorine When Present in Turpentine 354
SNIDER, J. B., AMBLER, J. A., AND BYALL, S. Impurities in White Sugars. II—Determination of Sulfates, Sulfites, and Aldehyde-Sulfites 339
SOMMER, H. H., AND GEBHARDT, H. T. Determination of Copper in Dairy Products 24
Residual-Current Measurements in Control of Metal Solution in Milk 414
STALEY, W. D., AND PARR, S. W. Determination of Sulfur by Means of Turbidimeter 66
Studies in Adiabatic Calorimetry 396
STAUD, C. J., MURRAY, T. F., JR., AND GRAY, H. LEB. Acid Value of Cellulose Fatty Acid Esters and Rapid Analysis of Certain Cellulose Acetates 269
STONE, IRWIN. Method for Increasing Sensitivity of Certain Chemical Test Reactions 325
STOVER, N. M., AND SANDIN, R. B. Use of Boric Acid in Micro-Kjeldahl Determination of Nitrogen 240
STUGART, RALPH. Determination of Iron in Milk and Other Biological Materials 390
SUNIER, A. A., AND WHITE, C. M. Modified Vacuum Regulator 259

TABERN, D. L., AND SHELBERG, E. F. Determination of Sodium in Organic Compounds. Use of Uranyl Acetate Method 278
THAYER, L. A. Colorimetric Determination of Silica. [*See* IND. ENG. CHEM., Anal. Ed., **2**, 276 (1930)] 118
THOMPSON, J. J., AND WILLARD, H. H. Volumetric and Gravimetric Determination of Mercury as Periodate 398
Volumetric Determination of Manganese after Oxidation by Periodate 399
THOMPSON, T. G., AND BONNAR, R. U. Buffer Capacity of Sea Water 393
TOURTELLOTTE, DEE, AND RASK, O. S. Spectrographic Determination of Aluminum in Biological Ashes 97
TRAUTZ, O. R., AND NIEDERL, J. B. Absolute Determination of Nitrogen in Organic Compounds 151
TREMAIN, H. E. New Test for Halogens 225
TRUSTY, A. W., AND SCHARNAGEL, A. R. Determination of Hydrogen Sulfide in Refinery Still Gases 29
TURNER, W. D. Improved Absorption Tube for Combustion Analysis 63

VAUGHN, T. H., AND NIEUWLAND, J. A. Determination of Organic Halogen by Liquid Ammonia-Sodium Process 274
VOLLMAR, R. C. Quantitative Determination of Pyrethrin I 110

WARD, J. S., AND GEHMAN, S. D. Microturbidimeter for Determination of Rubber Content of Latex 300
WEINBERGER, WOLTOR. Method for Determination of Small Quantities of Paraform in Various Mixtures 357
Test for Aldehydes Using Dimethylcyclohexanedione 365
WELLMAN, V. E. All-Glass Steam Distillation Apparatus for Analytical Purposes 281
WERKMAN, C. H., AND OSBURN, O. L. Determination of Butyl and Ethyl Alcohols in Mixtures 387
Determination of Organic Acids. V—Application of Partition Method to Quantitative Determination of Acetic, Propionic, and Butyric Acids in Mixture 264
WHITE, C. M., AND SUNIER, A. A. Modified Vacuum Regulator 259
WICHERS, EDWARD, ISAACS, AARON, AND SCHOONOVER, I. C. Two Hundred Reagent Chemicals—Good and Bad 227
WILEY, R. C. Gravimetric and Direct Volumetric Determination of Cadmium 14
Separation of Calcium and Magnesium by Molybdate Method 127
WILKENS, G. A., HIXSON, A. W., WORK, L. T., ALESSANDRONI, H. V., AND CLIFFORD, G. E. Apparatus for Experimental Pyrolytic Production of Diphenyl 289
WILLARD, H. H., AND GIBSON, R. C. Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid. (Correction, 226) 88
AND THOMPSON, J. J. Volumetric and Gravimetric Determination of Mercury as Periodate 398
Volumetric Determination of Manganese after Oxidation by Periodate 399
WILLIAMS, J. B., BROWN, D. J., AND MOSS, J. A. Determination of Lead as Chromate in Presence of Perchloric Acid 134
WIRTEL, A. F., DEGROOTE, MELVIN, KEISER, BERNHARD, AND MONSON, L. T. Analysis of Fatty Modifications Obtained by Action of Sulfuric Acid 243
WISE, L. E., AND FAIRBROTHER, A. M. Chemistry of Wood—III. Part 1—Comparison of Two Methods for Determination of Lignin 253
AND HARLOW, W. M. Chemistry of Wood—III. Part 2—Comparison of Two Methods for Preparation of Lignin from Wood 254
WOOTEN, L. A., CLARKE, B. L., AND COMPTON, K. G. Potentiometric Titration in Non-Aqueous Solutions. I—Differential Method for Determining Oil Acidity 321
WORK, L. T., HIXSON, A. W., ALESSANDRONI, H. V., CLIFFORD, G. E., AND WILKENS, G. A. Apparatus for Experimental Pyrolytic Production of Diphenyl 289
WORTHINGTON, K. K., WITH HARING, M. M. Methods for Determining Solubilities of Some Fluosilicates 7

ZERBAN, F. W., AND SATTLER, LOUIS. Ash and Electrical Conductivity of Refined Cane Sugars 41
Conductometric Formula for Determining Ash in Both Raw and Refinery Sirups and Molasses 38
Studies on Turbidity in Sugar Products. I—Relation between Intensity of Tyndall Beam and Depth and Concentration of Solution 326
ZIMBON, E. Transparent Cellulose Covers for Nessler Comparison Tubes 356

SUBJECT INDEX

INDUSTRIAL AND ENGINEERING CHEMISTRY

ANALYTICAL EDITION

VOLUME 3—1931

ABRASION Resistance, Measurement of. I—Paints, Varnishes, and Lacquers. A. E. Schuh and E. W. Kern 72
Absorption, Micro-, Tube with Mercury Seals. R. T. K. Cornwell 4
Absorption Tube, Improved, for Combustion Analysis. W. D. Turner. 63
Acetone-Water Mixtures, Comparison of Solubilities of Calcium and Strontium *p*-Bromobenzoates in. J. C. Bailar, Jr 362
ACIDS:
Acetic, Benzidine Method for Determination of—in Lead Acetate. J. E. S. Han and T. L. Chu 379
Organic, Determination of. V—Application of Partition Method to Quantitative Determination of Acetic, Propionic, and Butyric—in Mixture. O. L. Osburn and C. H. Werkman 264
Potentiometric Determination of Acidity in Insulating Oils. R. N. Evans and J. E. Davenport 82
Relation of pH of Butter to Titratable Acidity. B. H. Nissen 374
Value of Cellulose Fatty Acid Esters. T. F. Murray, Jr., C. J. Staud, and H. LeB. Gray 269
Actinometer, Oxalic Acid–Uranyl Acetate, Application of—to Measurement of Sunlight Intensity in Connection with Photochemical Changes in Gasoline. L. C. Beard, Jr., and O. M. Reiff 280
Air, Practical Methods of Detecting and Estimating Methyl Chloride in Foods and. With Description of Modified Combustion Method. M. J. Martinek and W. C. Marti 408
Alcohol Replacing Gasoline in Brazil 76
Alcohol. *See kind of alcohol.*
Aldehydes, Test for—Using Dimethylcyclohexanedione. Woltor Weinberger 365
Alkalinity of Reclaimed Rubber, Determination of. H. F. Palmer and G. W. Miller 45
Alkaloids, Opium, as Reagents for Formaldehyde. C. C. Fulton 200
Alloys, Chrome-Nickel, Modified Ford-Williams Method for Manganese in. L. H. James 31
Alloy Steels. *See* Steels.
Aluminum, Determination of—in Ferrochromium and Chromium Metal. T. R. Cunningham 103
Aluminum, Spectrographic Determination of—in Biological Ashes. Dee Tourtellotte and O. S. Rask 97
Amaranth, Quantitative Estimation of—and Tartrazine in Food Color Mixture. O. L. Evenson and R. H. Nagel 260
American Oil Chemists' Society, Study of Official Method of Bleaching Test of. M. T. Sanders. (Correspondence) 226
Amino Acids, Effect of—upon Rotation of Glucose and Fructose and Significance to Determination of Sucrose by Double Polarization Methods. D. T. Englis and F. A. Dykins 17
AMMONIA:
Ammoniacal Fluoride Solutions, Electroanalytical Separations in. I—Separation of Copper from Arsenic and Antimony. N. H. Furman 217
Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium, Investigation of. W. W. Scott and S. M. Alldredge 32
Liquid—Sodium Process, Determination of Organic Halogen by. T. H. Vaughn and J. A. Nieuwland 274
See Latex.
Anemia, Pernicious, Copper Iron Compound Developed for 313
ASH:
Biological, Spectrographic Determination of Aluminum in. Dee Tourtellotte and O. S. Rask 97
Carbonate, Use of—Determination in Study of Possible Theoretical Brix Correction Factor for Approximation of Solids by Drying. Degree Brix–Total Solid Relationship. R. H. King 230
Conductometric Formula for Determining—in Both Raw and Refinery Sirups and Molasses. Louis Sattler and F. W. Zerban 38
Electrical Conductivity and—of Refined Cane Sugars. F. W. Zerban and Louis Sattler 41
Asphalt, Potentiometric Determination of Saponification Number of Mixtures of—and Drying Oils. J. V. Demarest and Wm. Rieman, 3rd 15
Autoclave, Simple Laboratory. H. A. Cassar 197

BALANCE, Modified, for Approximate and Quick Weighing. E. Karrer 112
Barium Chromate Method, Volumetric, for Sulfates. J. R. Andrews .. 361
Barium, Conductometric Titration of Sulfate and. I. M. Kolthoff and T. Kameda 129
Barium Fluosilicate Spray Residue, Determination of. R. H. Carter .. 146
Barium Hydroxide, Direct and Reverse Titration of Sulfuric Acid with. I. M. Kolthoff and E. B. Sandell 115
Barium Sulfate. Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium. W. W. Scott and S. M. Alldredge 32
Benzidine Method for Determination of Acetic Acid in Lead Acetate. J. E. S. Han and T. L. Chu 379
Biological Materials, Determination of Iron in Milk and. Ralph Stugart 390
Biological Products, Extractor for. C. L. Shrewsbury 320
Bleaching Test, Study of Official Method of American Oil Chemists' Society. M. T. Sanders. (Correspondence) 226
Boric Acid, Use of—in Micro-Kjeldahl Determination of Nitrogen. N. M. Stover and R. B. Sandin 240
Bottles, Gas-Washing, Comparative Efficiencies of. F. H. Rhodes and D. R. Rakestraw 143
Bromination with Potassium Bromide–Bromate Mixture, Some Factors in. Problems in Estimation of Unsaturated Hydrocarbons in Gases—III. H. S. Davis, G. S. Crandall, and W. E. Higbee, Jr ... 108
Bromine, Lots of—in Ocean 107
Bromine Method, Adaptation of—to Include Range of 1 to 75 p. p. m. in Determination of Phenols in Water Solution. J. A. Shaw 273
Bromine Method, Application of—in Determination of Phenols and Cresols. R. D. Scott 67
Buffers, Use of—in Determination of Color by Means of Titanium Trichloride—II. O. L. Evenson and R. H. Nagel 167
Butter. *See* Fats.
Butyl Alcohols, Determination of Ethyl and—in Mixtures. C. H. Werkman and O. L. Osburn 387

CADMIUM:
Detection of. J. S. Pierce and W. T. Forsee 188
Gravimetric and Direct Volumetric Determination of. R. C. Wiley. 14
Quantitative Separation of Copper and—by Reduction of Their Salts with Potassium Formate. E. I. Fulmer 257
Calcium *p*-Bromobenzoates, Comparison of Solubilities of Strontium and—in Acetone-Water Mixtures. J. C. Bailar, Jr 362
Calcium, Quantitative Determination of Magnesium, Phosphorus, and—in Feedstuffs and Cattle Excreta. H. P. Morris, J. W. Nelson, and L. S. Palmer 164
Calcium, Separation of—and Magnesium by Molybdate Method. R. C. Wiley 127
Calcium Sulfate. Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium. W. W. Scott and S. M. Alldredge 32
Calorimetry, Adiabatic, Studies in. S. W. Parr and W. D. Staley 396
CARBON:
Black, Measurement of Effect of—on Fluidity of Printing Ink. E. P. W. Kearsley and G. L. Roberts 310
Determination of—in Sewage and Industrial Wastes. F. W. Mohlman and G. P. Edwards 119
Elimination of Sulfur in—Determinations by Direct Combustion. W. H. Blatchley 13
Method for Analysis of Volatile Compounds Containing Hydrogen, Nitrogen, and. W. Scholl and R. O. E. Davis 276
See also Steels.
Carbon Dioxide of High Purity, Generator for Production of. E. J. Poth 202
Carbon Dioxide, Solid, in Laboratory Technic. D. H. Killeffer 386
Cell, Improved Hydrogen-Electrode, for Determination of pH. W. B. Bollen 203
Cellulose Acetates, Certain, Rapid Analysis of. T. F. Murray, Jr., C. J. Staud, and H. LeB. Gray 269
Cellulose Covers, Transparent, for Nessler Comparison Tubes. E. Zimbon 356
Cellulose Fatty Acid Esters. Acid Value of. T. F. Murray, Jr., C. J. Staud, and H. LeB. Gray 269
Chart, Alignment, for Estimating Viscosity-Gravity Constant of Petroleum Lubricating Oils. W. F. Houghton and J. A. Robb 144
Chemicals, Analytical Reagent, Recommended Specifications for. A. C. S. Committee on Analytical Reagents, W. D. Collins, Chairman 221
Chemicals, Two Hundred Reagent—Good and Bad. Edward Wichers, Aaron Isaacs, and I. C. Schoonover 227
Chlorine, Determination of Small Quantities of Sulfur and—When Present in Turpentine. W. C. Smith 354
Chromate. *See kind of chromate.*
Chromic Acid Method, Determination of Carbon in Sewage and Industrial Wastes by. F. W. Mohlman and G. P. Edwards 119
CHROMIUM:
Arc Spectrographic Estimation of—in Ruby. Jacob Papish and W. J. O'Leary 11
Determination of Aluminum in Ferrochromium and—Metal. T. R. Cunningham 103
Determination of—and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid. H. H. Willard and R. C. Gibson. (Correction, 226) 88
Volumetric Determination of—and Nickel in Same Solution. L. H. James 258
COAL:
Analysis of Light Oils from Low- and Intermediate-Temperature Carbonization. E. B. Kester and C. R. Holmes 292
Fusain. S. W. Parr, H. C. Hopkins, and D. R. Mitchell 64
Plastometer. New Instrument for Measuring Plastic Properties of. J. D. Davis 43
Portable Equipment for Crushing and Quartering Samples of—Coke, or Other Lumpy Materials. E. S. Pettyjohn 163
Virginia, Unit Studies on. F. H. Fish and J. A. Addlestone 155
Cobalt, Electrolytic Determination of. Dorothy H. Brophy 363
Coke. *See* Coal.
COLOR:
Food, Quantitative Estimation of Amaranth and Tartrazine in. O. L. Evenson and R. H. Nagel 260
Hydrogen-Ion Concentration and—of Lead Chromate Pigments. R. C. Ernst, E. Pragoff, Jr., and E. E. Litkenhous 174
Measurement of—in Solutions of White Sugars. J. A. Ambler and S. Byall 135
Standards, Glass, Notes on Use of—for Determination of Phosphorus by Deniges Colorimetric Method. H. D. Chapman 282

Use of Buffers in Determination of—by Means of Titanium Trichloride—II. O. L. Evenson and R. H. Nagel ... 167
Colorimeter, Photoelectric, Determination of Hydrogen-Ion Concentration with. R. H. Müller and H. M. Partridge ... 169
Colorimetric Determination of Silica. E. J. King; L. A. Thayer (Correspondence) ... 117
Colorimetric Method, Rapid, for Determination of Molybdenum in Plain Carbon and Alloy Steels. T. R. Cunningham and H. L. Hamner ... 106
COMBUSTION ANALYSIS:
Elimination of Sulfur in Carbon Determinations by Direct Combustion. W. H. Blatchley ... 13
Gas-Pressure Regulator, Simple and Easily Constructed. A. C. Robertson ... 383
Hydrocarbons, Three. K. A. Kobe ... 262
Improved Absorption Tube for. W. D. Turner ... 63
Modified Method, Description of, in Practical Methods of Detecting and Estimating Methyl Chloride in Air and Foods. M. J. Martinek and W. C. Marti ... 408
Modified Pipet for Slow. K. A. Kobe ... 159
CONDUCTOMETRIC DETERMINATIONS:
Ash and Electrical Conductivity of Refined Cane Sugars. F. W. Zerban and Louis Sattler ... 41
Estimation of Solids in Steam by Conductivity. J. K. Rummel ... 317
Formula for Determining Ash in Both Raw and Refinery Sirups and Molasses. Louis Sattler and J. W. Zerban ... 38
Titration of Sulfate and Barium. I. M. Kolthoff and T. Kameda ... 129
COPPER:
Determination of—in Dairy Products. H. T. Gebhardt and H. H. Sommer ... 24
Determination of—in Organic Matter. Stefan Ansbacher, R. E. Remington, and F. B. Culp ... 314
Iodide Method for. Bartholow Park ... 77
Iron Compound Developed for Pernicious Anemia ... 313
Quantitative Separation of—and Cadmium by Reduction of Their Salts with Potassium Formate. E. I. Fulmer ... 257
Separation of—from Arsenic and Antimony. Electroanalytical Separations in Ammoniacal Fluoride Solutions—I. N. H. Furman ... 217
Copper Fluosilicate. *See* Fluosilicates.
Cresols, Application of Bromine Method in Determination of Phenol and. R. D. Scott ... 67

DAIRY Products, Determination of Copper in. H. T. Gebhardt and H. H. Sommer ... 24
Density of Gems and Small Amounts of Solids, Device for Estimation of. E. W. Blank ... 9
Dextrose, Determination of—and Levulose in Honey by Use of Iodine-Oxidation Method. R. E. Lothrop and R. L. Holmes ... 334
Diastase, Taka-, Malt, and Pancreatic. Estimation of Diastatic Enzyme Preparations. Taichi Harada ... 1
Dimethylcyclohexanedione, Test for Aldehydes Using. Woltor Weinberger ... 365
Diphenyl, Apparatus for Experimental Pyrolytic Production of. A. W. Hixson, L. T. Work, H. V. Alessandroni, G. E. Clifford, and G. A. Wilkens ... 289
Dish for Toxicity Tests. A. S. Daniels ... 358
DISTILLATION:
Analysis, Precise Fractional, Apparatus and Methods for. New Method of Gas Analysis. W. J. Podbielniak ... 177
Apparatus, All-Glass Steam, for Analytical Purposes. V. E. Wellman ... 281
Flow Divider for Fractionation under Diminished Pressure. A. M. Schwartz and M. T. Bush ... 138
Free Ammonia Nitrogen from Buffered Solutions. M. S. Nichols and Marian E. Foote ... 311
Improved Gauze-Plate Laboratory Rectifying Column. S. Palkin ... 377
Kjeldahl—of Nitrogen, Use of Steam for. Jesse Green ... 160
Micro-Kjeldahl Method, Accurate and Adaptable, of Nitrogen Determination. W. F. Allen ... 239
Perchloric Acid as New Standard in Acidimetry. G. F. Smith and W. W. Koch ... 52
Stillhead for Laboratory Columns. E. B. Kester and R. Andrews ... 373
Vacuum, Dissociation of Concentrated Perchloric Acid during—at Moderately Low Pressures. New Method for Preparation of Anhydrous Perchloric Acid. O. E. Goehler and G. F. Smith ... 55
Vacuum, Purification of Perchloric Acid by. G. F. Smith and O. E. Goehler ... 48
Drugs, Manufacturers of—in Russia ... 224
Dumas, Micro-, Method, Determination of Nitrogen by. Microanalysis with Ordinary Balance. W. J. Saschek ... 198
Dust May Replace Oil as Source of Power ... 173
Dyes and Egg Albumin. New Substrates for Use in Detecting Proteolytic Activity. R. L. Jones ... 149

EGG Albumin and Dyes. New Substrates for Use in Detecting Proteolytic Activity. R. L. Jones ... 149
Electrodes, Low-Resistance Glass, Hydrogen-Ion Determinations with. G. R. Robertson ... 5
Electrodes, Quinhydrone, Continuous Measurement of pH with. C. C. Coons ... 402
ELECTROLYTIC DETERMINATION:
Anodic Precipitation of Lead Peroxide. M. L. Nichols ... 384
Of Cobalt. Dorothy H. Brophy ... 363
Of Lead as Lead Dioxide. W. T. Schrenk and P. H. Delano ... 27
Residual-Current Measurements in Control of Metal Solution in Milk. H. T. Gebhardt and H. H. Sommer ... 414
Enzyme Preparations, Diastatic, Estimation of. Taka-Diastase, Malt Diastase, and Pancreatic Diastase. Taichi Harada ... 1
Ethyl Alcohols, Determination of Butyl and—in Mixtures. C. H. Werkman and O. L. Osburn ... 387
Ethylene, Effect of Light on Determination of. J. L. Oberseider and J. H. Boyd, Jr. ... 123
Excreta, Cattle, Quantitative Determination of Calcium, Magnesium, and Phosphorus in Feedstuffs and. H. P. Morris, J. W. Nelson, and L. S. Palmer ... 164
Extractor. *See kind of extractor.*

FATS:
Butter, pH of, and Its Relation to Titratable Acidity. B. H. Nissen. 374
Determination of Smoking Point of. J. M. McCoy ... 347
See also Oils.
Feedstuffs, Quantitative Determination of Calcium, Magnesium, and Phosphorus in Cattle Excreta and. H. P. Morris, J. W. Nelson, and L. S. Palmer ... 164
Ferrochromium. *See* Chromium.
Ferrosilicons, 48 to 52 Per Cent, Indirect Estimation of Silicon in. G. T. Dougherty ... 158
Fertilizer Materials, Should a Change Be Made in Analytical Procedure for Evaluating Available Phosphoric Acid Content of? C. C. Howes and C. B. Jacobs ... 70
Fertilizers, Measurement of Drillability of. A. L. Mehring ... 34
Filtration Tube, Centrifugal, Further Applications of. E. L. Skau and L. F. Rowe ... 147
Fisheries, New Research Laboratory at Gloucester, Mass. ... 343
Float and Temperature Regulators, Glass. D. F. Othmer ... 139
Flow Divider for Fractionation under Diminished Pressure. A. M. Schwartz and M. T. Bush ... 138
Fluorine, Effect of Certain Forms of Silica on Determination of—by Volatilization Method. D. S. Reynolds and K. D. Jacob ... 371
Fluorine, Method for Determination of—in Phosphate Rock and Phosphatic Slags. D. S. Reynolds and K. D. Jacob ... 366
Fluosilicates, Methods for Determining Solubilities of. Katherine K. Worthington with M. M. Haring ... 7
Food Colors. *See* Color.
Food Industries Welcome Legal Standards ... 344
Foods, Practical Methods of Detecting and Estimating Methyl Chloride in Air and. With Description of Modified Combustion Method. M. J. Martinek and W. C. Marti ... 408
Ford-Williams Method, Modified. L. H. James ... 31
Formaldehyde, Hehner Test for. C. C. Fulton ... 199
Formaldehyde, Opium Alkaloids as Reagents for. C. C. Fulton ... 200
Fractionation. *See* Distillation.
Fructose, Determination of Glucose in Presence of—and Glycine by Iodometric Method. F. A. Dykins and D. T. Englis ... 21
Fructose, Effect of Amino Acids upon Rotation of Glucose and—and Significance to Determination of Sucrose by Double Polarization Methods. D. T. Englis and F. A. Dykins ... 17
Fusain. S. W. Parr, H. C. Hopkins, and D. R. Mitchell ... 64

GAS:
Analysis. Apparatus and Methods for Precise Fractional-Distillation Analysis. W. J. Podbielniak ... 177
Dry Method of Microanalysis of. F. E. Blacet and P. A. Leighton ... 266
Hydrocarbons, Gaseous, Analysis of. R. Rosen and A. E. Robertson ... 284
Method for Analysis of Volatile Compounds Containing Carbon, Hydrogen, and Nitrogen. W. Scholl and R. O. E. Davis ... 276
Pressure Regulator, Simple and Easily Constructed. A. C. Robertson ... 383
Problems in Estimation of Unsaturated Hydrocarbons in. III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture. H. S. Davis, G. S. Crandall, and W. E. Higbee, Jr. ... 108
Refinery Still, Determination of Hydrogen Sulfide in. A. R. Scharnagel and A. W. Trusty ... 29
Washing Bottles, Comparative Efficiencies of. F. H. Rhodes and D. R. Rakestraw ... 143
GASOLINE:
Alcohol Replacing—in Brazil ... 76
Aviation, Solubility of Water in. Elizabeth W. Aldrich ... 348
Photochemical Changes in, Application of Oxalic Acid–Uranyl Acetate Actinometer to Measurement of Sunlight Intensity in Connection with. L. C. Beard, Jr., and O. M. Reiff ... 280
Gems, Device for Estimation of Density of—and Small Amounts of Solids. E. W. Blank ... 9
Glassware, Chemical, Easy Method of Marking. K. H. Morkert and W. D. Hatfield ... 242
Glucose, Determination of—in Presence of Fructose and Glycine by Iodometric Method. F. A. Dykins and D. T. Englis ... 21
Glucose, Effect of Amino Acids upon Rotation of—and Fructose and Significance to Determination of Sucrose by Double Polarization Methods. D. T. Englis and F. A. Dykins ... 17
Glycerol, Determination of—in Greases. M. H. Pramme ... 232
Glycine, Determination of Glucose in Presence of Fructose and—by Iodometric Method. F. A. Dykins and D. T. Englis ... 21
Gravity-Viscosity Constant of Petroleum Lubricating Oils, Alignment Chart for Estimating. W. F. Houghton and J. A. Robb ... 144
Greases, Determination of Glycerol in. M. H. Pramme ... 232
Gums, Common, Method for Identification of. M. B. Jacobs and L. Jaffe ... 210

HALOGEN, Organic, Determination of—by Liquid Ammonia-Sodium Process. T. H. Vaughn and J. A. Nieuwland ... 274
Halogens, New Test for. H. E. Tremain ... 225
Hehner Test for Formaldehyde. C. C. Fulton ... 199
Hemicelluloses, Notes on Determination of. R. C. Malhotra ... 161
Honey, Determination of Dextrose and Levulose in—by Use of Iodine-Oxidation Method. R. E. Lothrop and R. L. Holmes ... 334
HYDROCARBONS:
Analysis of Three—by Combustion. K. A. Kobe ... 262
Effect of Light on Determination of Ethylene. J. L. Oberseider and J. H. Boyd, Jr. ... 123
Gaseous, Analysis of. R. Rosen and A. E. Robertson ... 284
Olefin, Aromatic, and Paraffin, Determination of—in Neutral Oil from Coal Tar. E. B. Kester and W. D. Pohle ... 294
Unsaturated, Problems in Estimation of—in Gases. III—Some Factors in Bromination with Potassium Bromide–Bromate Mixture. H. S Davis, G. S. Crandall, and W. E. Higbee, Jr. ... 108
Hydrogen, Method for Analysis of Volatile Compounds Containing Carbon, Nitrogen and. W. Scholl and R. O. E. Davis ... 276
HYDROGEN-ION DETERMINATIONS:
Ammonia Latex. J. McGavack and J. S. Rumbold ... 94
Butter and Its Relation to Titratable Acidity. B. H. Nissen ... 374
Color of Lead Chromate Pigments and. R. C. Ernst, E. Pragoff, Jr., and E. E. Litkenhous ... 174
Continuous Measurement of—with Quinhydrone Electrodes. C. C. Coons ... 402
Hydrogen-Electrode Cell, Improved, for Determination of. W. B. Bollen ... 203
Photoelectric Colorimeter for. R. H. Müller and H. M. Partridge. 169
Use of Wide-Range Indicators for. F. R. McCrumb ... 233
With Low-Resistance Glass Electrodes. G. R. Robertson ... 5
Hydrogen Sulfide, Determination of—in Refinery Still Gases. A. R. Scharnagel and A. W. Trusty ... 29

IGNITION Losses in Potash Analyses of Triple Superphosphate Mixtures. L. B. Lockhart ... 407
Indicators, Wide-Range, Use of—for pH Determination. F. R. McCrumb ... 233
Ink, Printing, Measurement of Effect of Carbon Black on Fluidity of. E. P. W. Kearsley and G. L. Roberts ... 310
Insecticides. Determination of Barium Fluosilicate Spray Residue. R. H. Carter ... 146
Iodide Method for Copper. Bartholow Park ... 77
Iodine, Oxidation of Ferrous Iron by—in Presence of Phosphate and Non-Existence of Ferriphosphate Complex. W. D. Bonner and Hendrick Romeyn, Jr. ... 85
Iodometric Method, Determination of Glucose in Presence of Fructose and Glycine by. F. A. Dykins and D. T. Englis ... 21
IRON:
Copper Compound Developed for Pernicious Anemia ... 313
Determination of—in Milk and Other Biological Materials. Ralph Stugart ... 390
Ferrous, Oxidation of—by Iodine in Presence of Phosphate and Non-Existence of Ferriphosphate Complex. W. D. Bonner and Hendrick Romeyn, Jr. ... 85
Thiosulfate Titrations of Small Amounts of—in Glass Sands. L. B. Skinner ... 411

KJELDAHL METHOD:
Distillation of Nitrogen, Use of Steam for. Jesse Green ... 160
Micro-, Accurate and Adaptable, for Determination of Nitrogen. W. F. Allen ... 239
Microdetermination, Use of Boric Acid in—of Nitrogen. N. M. Stover and R. B. Sandin ... 240
Use of Selenium as Catalyst in Determination of Nitrogen by. M. F. Lauro ... 401

LACQUERS. *See* Paints.
Latex Ammonia, Determination of pH of. J. McGavack and J. S. Rumbold ... 94
Latex, Microturbidimeter for Determination of Rubber Content of. S. D. Gehman and J. S. Ward ... 300
Leaching, Continuous, Apparatus for—with Suction. J. F. Fudge ... 114
Lead Acetate, Benzidine Method for Determination of Acetic Acid in. J. E. S. Han and T. L. Chu ... 379
Lead Chromate, Determination of Lead as—in Presence of Perchloric Acid. D. J. Brown, J. A. Moss, and J. B. Williams ... 134
Lead Chromate Pigments, Hydrogen-Ion Concentration and Color of. R. C. Ernst, E. Pragoff, Jr., and E. E. Litkenhous ... 174
Lead, Determination of—as Chromate in Presence of Perchloric Acid. D. J. Brown, J. A. Moss, and J. B. Williams ... 134
Lead, Electrolytic Determination of—as Lead Dioxide. W. T. Schrenk and P. H. Delano ... 27
Lead Fluosilicate. *See* Fluosilicates.
Lead Peroxide, Anodic Precipitation of. M. L. Nichols ... 384
Lead Sulfate. Investigation of Ammonium Acetate Separation of Sulfates of Lead, Barium, and Calcium. W. W. Scott and S. M. Alldredge ... 32
Levulose, Determination of—and Dextrose in Honey by Use of Iodine-Oxidation Method. R. E. Lothrop and R. L. Holmes ... 334
Light, Effect of—on Determination of Ethylene. J. L. Oberseider and J. H. Boyd, Jr. ... 123
Lignin, Comparison of Two Methods for Determination of. Chemistry of Wood—III, Part 1. L. E. Wise and A. M. Fairbrother ... 253
Lignin, Comparison of Two Methods for Preparation of—from Wood. Chemistry of Wood—III, Part 2. W. M. Harlow and L. E. Wise ... 254

MAGNESIUM, Quantitative Determination of Calcium, Phosphorus, and—in Feedstuffs and Cattle Excreta. H. P. Morris, J. W. Nelson, and L. S. Palmer ... 164
Magnesium, Separation of Calcium and—by Molybdate Method. R. C. Wiley ... 127
Magnesium Fluosilicate. *See* Fluosilicates.
Malt Diastase. *See* Diastase.
Manganese, Modified Ford-Williams Method for. L. H. James ... 31
Manganese, Volumetric Determination of—after Oxidation by Periodate. H. H. Willard and J. J. Thompson ... 399
Melting Point Apparatus, Electrically-Heated. C. E. Sando ... 65
Mercury, Volumetric and Gravimetric Determination of—as Periodate. H. H. Willard and J. J. Thompson ... 398
Metal, Residual-Current Measurements in Control of—Solution in Milk. H. T. Gebhardt and H. H. Sommer ... 414
Methyl Chloride, Practical Methods of Detecting and Estimating—in Air and Foods. With Description of Modified Combustion Method. M. J. Martinek and W. C. Marti ... 408
MICROANALYSIS:
Copper Determination in Organic Matter. Stefan Ansbacher, R. E. Remington, and F. B. Culp ... 314
Dry Method of—of Gases. F. E. Blacet and P. A. Leighton ... 266
With an Ordinary Balance. I—Determination of Nitrogen by Micro-Dumas Method. W. J. Saschek ... 198
Microgravimetric Analysis, Improved Technic for. P. L. Kirk and Roderick Craig ... 345
Microturbidimeter for Determination of Rubber Content of Latex. S. D. Gehman and J. S. Ward ... 300
MILK:
Determination of Iron in—and Other Biological Materials. Ralph Stugart ... 390
Residual-Current Measurements in Control of Metal Solution in. H. T. Gebhardt and H. H. Sommer ... 414
See also Dairy Products.
Mill for Small Samples. W. H. Cook, E. P. Griffing, and C. L. Alsberg ... 102
Mineral, Production in Alaska in 1930 ... 40
Moisture Content of Liquid Sulfur Dioxide. A. K. Scribner ... 255
Molybdate Method, Separation of Calcium and Magnesium by. R. C. Wiley ... 127
Molybdenum, Rapid Colorimetric Method for Determination of—in Plain Carbon and Alloy Steels. T. R. Cunningham and H. L. Hamner ... 106

NICKEL, Volumetric Determination of Chromium and—in Same Solution. L. H. James ... 258
NITROGEN:
Absolute Determination of—in Organic Compounds. Pregl's Micro-Method. O. R. Trautz and J. B. Niederl ... 151
Ammonia, Free, Distillation of—from Buffered Solutions. M. S. Nichols and M. E. Foote ... 311
Determination of—by Micro-Dumas Method. Microanalysis with Ordinary Balance—I. W. J. Saschek ... 198
Method for Analysis of Volatile Compounds Containing Carbon, Hydrogen, and. W. Scholl and R. O. E. Davis ... 276
Micro-Kjeldahl Method, Accurate and Adaptable, for Determination of. W. F. Allen ... 239
Oxides (except Nitrous Oxide) in Low Concentrations, Determination of. A. G. Francis and A. T. Parsons; J. Piccard, E. G. Peterson, and C. D. Bitting. (Correspondence) ... 225
Use of Boric Acid in Micro-Kjeldahl Determination of. N. M. Stover and R. B. Sandin ... 240
Use of Selenium as Catalyst in Determination of—by Kjeldahl Method. M. F. Lauro ... 401
Use of Steam for Kjeldahl Distillation. Jesse Green ... 160

OCEAN. *See* Water, Sea.
OIL:
Acidity, Differential Method for Determining. Potentiometric Titration in Non-Aqueous Solutions—I. B. L. Clarke, L. A. Wooten, and K. G. Compton ... 321
Analysis of Fatty Modifications Obtained by Action of Sulfuric Acid. Melvin DeGroote, Bernhard Keiser, A. F. Wirtel, and L. T. Monson ... 243
Drying, Potentiometric Determination of Saponification Number of Mixtures of Asphalt and. J. V. Demarest and Wm. Rieman, 3rd ... 15
Dust May Replace—as Source of Power ... 173
Insulating, Potentiometric Determination of Acidity in. R. N. Evans and J. E. Davenport ... 82
Light, Analysis of—from Low- and Intermediate-Temperature Carbonization. E. B. Kester and C. R. Holmes ... 292
Measurement of Rate of Formation of Oxidative Decomposition Products in Fats and. D. P. Grettie and R. C. Newton ... 171
See also Petroleum.
Opium Alkaloids. *See* Alkaloids.
Organic Matter, Copper Determination in. Stefan Ansbacher, R. E. Remington, and F. B. Culp ... 314
Oxides of Nitrogen (except Nitrous Oxide) in Low Concentration, Determination of. A. G. Francis and A. T. Parsons; J. Piccard, E. G. Peterson, and C. D. Bitting. (Correspondence) ... 225
Oxonium Perchlorate as Reference Standard for Construction of Specific Gravity–Percentage Composition Table for Strong Perchloric Acid Solutions. G. F. Smith and O. E. Goehler ... 61
Oxonium Structure of Hydrated Perchloric Acid. G. F. Smith and O. E. Goehler ... 58

PAINT, Expansion of—Industry in India ... 360
Painting, Wood—Conference, Proceedings of ... 118
Paints, Varnishes, and Lacquers. Measurement of Abrasion Resistance—I. A. E. Schuh and E. W. Kern ... 72
Pancreatic Diastase. *See* Diastase.
Paraform, Method for Determination of Small Quantities of—in Various Mixtures. Woltor Weinberger ... 357
Partition Method, Application of—to Quantitative Determination of Acetic, Propionic, and Butyric Acids in Mixture. Determination of Organic Acids—V. O. L. Osburn and C. H. Werkman ... 264
PERCHLORIC ACID:
As New Standard in Acidimetry. G. F. Smith and W. W. Koch ... 52
Concentrated, Dissociation of—during Vacuum Distillation at Moderately Low Pressures. New Method for Preparation. O. E. Goehler and G. F. Smith ... 55
Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with. H. H. Willard and R. C. Gibson. (Correction, 226) ... 88
Determination of Lead as Chromate in Presence of. D. J. Brown, J. A. Moss, and J. B. Williams ... 134
Hydrated, Oxonium Structure of. G. F. Smith and O. E. Goehler ... 58
Purification of—by Vacuum Distillation. G. F. Smith and O. E. Goehler ... 48
Strong Solutions, Oxonium Perchlorate as Reference Standard for Construction of Specific Gravity–Percentage Composition Table for. G. F. Smith and O. E. Goehler ... 61
Periodate. *See kind of periodate.*
Petroleum. Determination of Olefin, Aromatic, and Paraffin Hydrocarbons in Neutral Oil from Coal Tar. E. B. Kester and W. D. Pohle ... 294
Petroleum Lubricating Oils, Alignment Chart for Estimating Viscosity–Gravity Constant of. W. F. Houghton and J. A. Robb ... 144
Phenol, Application of Bromine Method in Determination of—and Cresols. R. D. Scott ... 67
Phenols, Determination of—in Water Solution. Adaptation of Bromine Method to Include Range of 1 to 75 p. p. m. J. A. Shaw ... 273
Phosgene, Quantitative Determination of. J. C. Olsen, G. E. Ferguson, V. J. Sabetta, and Leopold Scheflan ... 189
Phosphate, Oxidation of Ferrous Iron by Iodine in Presence of—and Non-Existence of Ferriphosphate Complex. W. D. Bonner and Hendrick Romeyn, Jr. ... 85
Phosphate Rock and Slags, Method for Determination of Fluorine in. D. S. Reynolds and K. D. Jacob ... 366
Phosphates, Determination of—in Presence of Silica in Boiler Water. E. W. Scarritt ... 23
Phosphoric Acid, Availability of—in Ammoniated Superphosphates. K. Kitsuta and R. M. Salter ... 331
Phosphoric Acid, Should a Change Be Made in Analytical Procedure for Evaluating Available—Content of Fertilizer Materials? C. C. Howes and C. B. Jacobs ... 70
PHOSPHORUS:
Determination of. Impurities in White Sugars—I. S. Byall and J. A. Ambler ... 136
Notes on Use of Glass Color Standards for Determination of—by Deniges Colorimetric Method. H. D. Chapman ... 282
Quantitative Determination of Calcium, Magnesium, and—in Feedstuffs and Cattle Excreta. H. P. Morris, J. W. Nelson, and L. S. Palmer ... 164
Photochemistry. Application of Oxalic Acid–Uranyl Acetate Actinometer to Measurement of Sunlight Intensity in Connection with Photochemical Changes in Gasoline. L. C. Beard, Jr., and O. M. Reiff ... 280

Photoelectric Colorimeter. *See* Colorimeter.
Pigments. *See kind of pigment.*
Pipet, Modified Slow-Combustion. K. A. Kobe..... 159
Plants. Notes on Determination of Hemicelluloses. R. C. Malhotra. 161
Plastometer. New Instrument for Measuring Plastic Properties of Coal. J. D. Davis..... 43
Polarization, Double, Effect of Amino Acids upon Rotat on of Glucose and Fructose and Significance to Determination of Sucrose by—Methods. D. T. Englis and F. A. Dykins..... 17
Potash, Ignition Losses in—Analyses of Triple Superphosphate Mixtures. L. B. Lockhart..... 407
Potassium Bromide–Bromate Mixture, Some Factors in Bromination with. Problems in Estimation of Unsaturated Hydrocarbons in Gases—III. H. S. Davis, G. S. Crandall, and W. E. Higbee, Jr... 108
Potassium Ferrocyanide, Stability of—Solutions. I. M. Kolthoff and E. A. Pearson..... 381
Potassium Formate, Quantitative Separation of Copper and Cadmium by Reduction of Their Salts with. E. I. Fulmer..... 257
Potassium, Quantitative Determination of—by Sodium Cobaltinitrite Method. P. J. Van Rysselberge..... 3
Potassium, Rapid Volumetric Method for Determination of. Loyal Clarke and J. M. Davidson..... 324
POTENTIOMETRIC DETERMINATIONS:
Acidity in Insulation Oils. R. N. Evans and J. E. Davenport..... 82
Saponification Number of Mixtures of Asphalt and Drying Oils. J. V. Demarest and Wm. Rieman, 3rd..... 15
Titration in Non-Aqueous Solutions. I—Differential Method for Determining Oil Acidity. B. L. Clarke, L. A. Wooten, and K. G. Compton..... 321
Powders, Fine, Accurate Air Separator for. P. S. Roller..... 212
Power, Dust May Replace Oil as Source of..... 173
Pregl's Micro-Method of Absolute Determination of Nitrogen in Organic Compounds. O. R. Trautz and J. B. Niederl..... 151
Protein, New Conversion Factors for..... 376
Proteolytic Activity, New Substrates for Use in Detecting. R. L. Jones..... 149
Pyrethrin I, Quantitative Determination of. R. C. Vollmar..... 110
Pyrolysis. Apparatus for Experimental Pyrolytic Production of Diphenyl. A. W. Hixson, L. T. Work, H. V. Alessandroni, G. E. Clifford, and G. A. Wilkens..... 289

QUINHYDRONE Electrodes. *See* Electrodes.

REAGENT Chemicals, Analytical, Recommended Specifications for. A. C. S. Committee on Analytical Reagents, W. D. Collins, Chairman..... 221
Reagent Chemicals, Two Hundred—Good and Bad. Edward Wichers, Aaron Isaacs, and I. C. Schoonover..... 227
Reagents. Method for Increasing Sensitivity of Certain Chemical Test Reactions. Irwin Stone..... 325
Rectifying Column, Improved Gauze-Plate Laboratory. S. Palkin... 377
Regulators. *See kind of regulator.*
Resins, Synthetic, Methods for Detection and Identification of. T. F. Bradley..... 304
RUBBER:
Microturbidimeter for Determination of—Content of Latex. S. D. Gehman and J. S. Ward..... 300
New Autographic Machine for Testing Tensile Properties of. G. J. Albertoni..... 236
Reclaimed, Determination of Alkalinity of. H. F. Palmer and G. W. Miller..... 45
Scorching, and Other Plasticity Changes in—Compounds on Heating. E. O. Dieterich and J. M. Davies..... 297
Threads, Graphical Tensile-Testing Machine for. S. H. Hahn and E. O. Dieterich..... 218
Ruby, Arc Spectrographic Estimation of Chromium in. Jacob Papish and W. J. O'Leary..... 11

SANDS, Glass, Thiosulfate Titrations of Small Amounts of Iron in. L. B. Skinner..... 411
Selenium, Use of—as Catalyst in Determination of Nitrogen by Kjeldahl Method. M. F. Lauro..... 401
Separator, Accurate Air, for Fine Powders. P. S. Roller..... 212
Sewage, Determination of Carbon in—and Industrial Wastes. F. W. Mohlman and G. P. Edwards..... 119
SILICA:
Colorimetric Determination of. L. A. Thayer; E. J. King. (Correspondence)..... 117
Determination of Phosphates in Presence of—in Boiler Water. E. W. Scarritt..... 23
Effect of Certain Forms of—on Determination of Fluorine by Volatilization Method. D. S. Reynolds and K. D. Jacob..... 371
Silicon, Indirect Estimation of—in 48 to 52 Per Cent Ferrosilicons. G. T. Dougherty..... 158
Sludge Ripeness Studies. E. L. Pearson and A. M. Buswell..... 359
Soap, Some Factors Influencing—Tests for Hardness. R. H. Kean and H. Gustafson..... 355
SODIUM:
Determination of—in Organic Compounds. Use of Uranyl Acetate Method. D. L. Tabern and E. F. Shelberg..... 278
Determination of Organic Halogen by Liquid Ammonia—Process. T. H. Vaughn and J. A. Nieuwland..... 274
Irregularities in—Determination by Sodium Sulfate Method. G. W. Collins..... 291
Sodium Cobaltinitrite Method, Quantitative Determination of Potassium by. P. J. Van Rysselberge..... 3
Sodium Fluosilicate. *See* Fluosilicates.
SOLIDS:
Device for Estimation of Density of Gems and Small Amounts of. E. W. Blank..... 9
Estimation of—in Steam by Conductivity. J. K. Rummel..... 317
Study of Possible Theoretical Brix Correction Factor for Approximation of—by Drying Using Carbonate Ash Determination. A Degree Brix–Total Solid Relationship. R. H. King..... 230
Solubilities of Calcium and Strontium *p*-Bromobenzoates in Acetone-Water Mixtures, Comparison of. J. C. Bailar, Jr..... 362
Solutions, Non-Aqueous, Potentiometric Titration in. I—Differential Method for Determining Oil Acidity. B. L. Clarke, L. A. Wooten, and K. G. Compton..... 321
Solutions, Potassium Ferrocyanide, Stability of. I. M. Kolthoff and E. A. Pearson..... 381
Soxhlet Extractor, Large-Scale. S. A. Lough..... 344
SPECTROGRAPHIC ANALYSES:
Aluminum in Biological Ashes. Dee Tourtellotte and O. S. Rask.... 97
Arc Spectrographic Estimation of Chromium in Ruby. Jacob Papish and W. J. O'Leary..... 11
Spectrophotometer, Measurement of Turbidity with. With Especial Reference to Sugarhouse Products. R. T. Balch..... 124
Starch Solutions, Measurement of Consistency of. J. C. Ripperton... 152
STEAM:
Distillation Apparatus, All-Glass, for Analytical Purposes. V. E. Wellman..... 281
Estimation of Solids in—by Conductivity. J. K. Rummel..... 317
Use of—for Kjeldahl Distillation of Nitrogen. Jesse Green..... 160
Steels, Alloy and Plain Carbon, Determination of Zirconium in. T. R. Cunningham and R. J. Price..... 105
Steels, Alloy and Plain Carbon, Rapid Colorimetric Method for Determination of Molybdenum in. T. R. Cunningham and H. L. Hamner..... 106
Stillhead. *See* Distillation.
Strontium *p*-Bromobenzoates, Comparison of Solubilities of Calcium and—in Acetone-Water Mixtures. J. C. Bailar, Jr..... 362
Substrates, New, for Use in Detecting Proteolytic Activity. R. L. Jones..... 149
Sucrose, Effect of Amino Acids upon Rotation of Glucose and Fructose and Significance to Determination of—by Double Polarization Methods. D. T. Englis and F. A. Dykins..... 17
SUGAR:
Cane, Refined, Ash and Electrical Conductivity of. F. W. Zerban and Louis Sattler..... 41
Conductometric Formula for Determining Ash in Both Raw and Refinery Sirups and Molasses. Louis Sattler and F. W. Zerban... 38
Degree Brix–Total Solid Relationship. Study of Possible Theoretical Brix Correction Factor for Approximation of Solids by Drying Using Carbonate Ash Determination. R. H. King..... 230
Measurement of Turbidity with Spectrophotometer. With Especial Reference to Sugarhouse Products. R. T. Balch..... 124
Studies on Turbidity in—Products. I—Relation between Intensity of Tyndall Beam and Depth and Concentration of Solution. F. W. Zerban and Louis Sattler..... 326
White, Impurities in.
I—Determination of Phosphorus. S. Byall and J. A. Ambler..... 136
II—Determination of Sulfates, Sulfites, and Aldehyde-Sulfites. J. A. Ambler, J. B. Snider, and S. Byall..... 339
III—Determination of Labile Organic Sulfur. J. A. Ambler..... 341
White, Measurement of Color in Solutions of. J. A. Ambler and S. Byall..... 135
See also kind of sugar.
SULFATES:
Conductometric Titration of Barium and. I. M. Kolthoff and T. Kameda..... 129
Determination of Sulfites, Aldehyde-Sulfites, and. Impurities in White Sugars—II. J. A. Ambler, J. B. Snider, and S. Byall..... 339
Volumetric Barium Chromate Method for. J. R. Andrews..... 361
SULFUR:
Determination of—by Means of Turbidimeter. S. W. Parr and W. D. Staley..... 66
Determination of Small Quantities of Chlorine and—When Present in Turpentine. W. C. Smith..... 354
Elimination of—in Carbon Determinations by Direct Combustion. W. H. Blatchley..... 13
Labile Organic, Determination of. Impurities in White Sugars—III. J. A. Ambler..... 341
Sulfur Dioxide, Liquid, Moisture Content of. A. K. Scribner..... 255
Sulfuric Acid, Analysis of Fatty Modifications Obtained by Action of. Melvin DeGroote, Bernhard Keiser, A. F. Wirtel, and L. T. Monson. 243
Sulfuric Acid, Direct and Reverse Titration of—with Barium Hydroxide. I. M. Kolthoff and E. B. Sandell..... 115
Sunlight. *See* Photochemistry.

TAKA-DIASTASE. *See* Diastase.
Tar, Coal, Determination of Olefin, Aromatic, and Paraffin Hydrocarbons in Neutral Oil from. E. B. Kester and W. D. Pohle..... 294
Tartrazine, Quantitative Estimation of Amaranth and—in Food Color Mixture. O. L. Evenson and R. H. Nagel..... 260
Temperature and Float Regulators, Glass. D. F. Othmer..... 139
Tensile-Testing Machine, Graphical, for Rubber Threads. S. H. Hahn and E. O. Dieterich..... 218
Tensile-Testing Machine, New Autographic, for Properties of Rubber. G. J. Albertoni..... 236
Thermostat, Low-Temperature. H. W. Foote and Gosta Akerlof.... 389
Thiosulfate Titrations of Small Amounts of Iron in Glass Sands. L. B. Skinner..... 411
Titanium Trichloride, Use of Buffers in Determination of Color by Means of—II. O. L. Evenson and R. H. Nagel..... 167
Toxicity Tests, Dish for. A. S. Daniels..... 358
Turbidimeter, Determination of Sulfur by Means of. S. W. Parr and W. D. Staley..... 66
Turbidity, Measurement of—with a Spectrophotometer. With Especial Reference to Sugarhouse Products. R. T. Balch..... 124
Turbidity, Studies on—in Sugar Products. I—Relation between Intensity of Tyndall Beam and Depth and Concentration of Solution. F. W. Zerban and Louis Sattler..... 326
Turpentine, Determination of Small Quantities of Sulfur and Chlorine When Present in. W. C. Smith..... 354

ULTRA-VIOLET Plant Installation, World's Largest..... 133
Uranyl Acetate, Use of—Method in Determination of Sodium in Organic Compounds. D. L. Tabern and E. F. Shelberg..... 278

VACUUM Regulator, Modified. A. A. Sunier and C. M. White..... 259
Vanadium, Determination of Chromium and—in Ores and Alloys after Oxidation with Perchloric Acid. H. H. Willard and R. C. Gibson. (Correction, 226)..... 88
Varnishes. *See* Paints.
Viscosity-Gravity Constant of Petroleum Lubricating Oils, Alignment Chart for Estimating. W. F. Houghton and J. A. Robb..... 144

WASTES, Industrial, Determination of Carbon in Sewage and. F. W. Mohlman and G. P. Edwards..... 119
WATER:
Analysis, Interpretation of. D. S. McKinney..... 192
Boiler, Determination of Phosphates in Presence of Silica in. E. W. Scarritt..... 23
Hardness, Some Factors Influencing Soap Tests for. R. H. Kean and H. Gustafson..... 355
Phenols in—Solution, Determination of. Adaptation of Bromine Method to Include Range of 1 to 75 p. p. m. J. A. Shaw..... 273
Sea:
Buffer Capacity of. T. G. Thompson and R. U. Bonnar..... 393
Lots of Bromine in..... 107
Proposed Modification of Oxygen Consumed Method for Determination of—Pollution. H. K. Benson and J. F. G. Hicks, Jr.. 30
Solubility of—in Aviation Gasolines. Elizabeth W. Aldrich..... 348
Wood, Chemistry of—III.
Part 1—Comparison of Two Methods for Determination of Lignin. L. E. Wise and A. M. Fairbrother..... 253
Part 2—Comparison of Two Methods for Preparation of Lignin from Wood. W. M. Harlow and L. E. Wise..... 254
Wood Painting Conference, Proceedings of..... 118

ZINC Fluosilicate. *See* Fluosilicates.
Zirconium, Determination of—in Plain Carbon and Alloy Steels. T. R. Cunningham and R. J. Price..... 105

PISL-11
540.5
1931 J82511
v.3
Industrial and engineering
chemistry.
Oct2241 25/3 256692

PISL-14
COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF PUBLIC INSTRUCTION
STATE LIBRARY
HARRISBURG
540.5
J
K82511
v.3
1931
In case of failure to return the books the borrower agrees to pay the original price of the same, or to replace them with other copies. The last borrower is held responsible for any mutilation.
Return this book on or before the last date stamped below. 256692
Oct2241